

THE INSTITUTE OF PAPER CHEMISTRY

Appleton, Wisconsin

STRESS CORROSION CRACKING OF CONTINUOUS  
DIGESTERS FOR KRAFT PULPING

Project 3544

A Final Report

to the

DIGESTER CRACKING RESEARCH COMMITTEE

January, 1983

SCC in Alkaline Sulfide Media	68
V. STATISTICS OF CRACKING IN CONTINUOUS DIGESTERS	74
Introduction	74
Kamyr Continuous Digester Systems	77
Digester Fabrication	83
Cracking Characteristics in Kamyr Continuous Digesters	89
Cracking Statistics	91
Distribution of Cracking	92
Crack Morphology	92
Cracking in Base Metal	93
Cracking at the Cone Transition Weld	93
Deep Cracking ( $> 1/2"$ )	94
Impregnation Vessel Versus Digester Cracking	94
Cracking Outside of the Impregnation Zone	95
Nozzle Cracking	95
Vertical Welds versus Horizontal Welds	96
Average Crack Penetration	96
Onset of Cracking	97
Metallography	97
Nondestructive Examination	98
Summary	101
Digester Cracking Versus Fabrication Variables	101
Digester Cracking Versus Operation	117
Acid Cleaning	118
Wood Species	120
Chip Versus Sawdust Digesters	123
Vapor Phase/Two Vessel Systems	123

White Liquor Characteristics Versus Cracking	124
Detailed Questionnaire Results at Six Selected Mills	129
SUMMARY	134
VI. REMEDIES FOR VESSEL CRACKING	135
Introduction	135
Repair by Grinding	136
Repair by Welding	136
Crack Prevention by Shot Peening	139
Crack Prevention by Stainless Alloy Overlays	140
Crack Prevention by Thermal Spray Coatings	142
Thermal Stress Relief in situ	143
Anodic Protection	143
VII. CHEMISTRY AND ELECTROCHEMISTRY OF KRAFT LIQUORS AT SELECTED MILLS	145
Introduction	145
Experimental Approach	146
Objective	146
Mill Site Selection	147
Liquor Sampling Site	148
Apparatus	151
Electrode Materials	156
Grab Sampling	160
Chemical Analysis	160
Procedure	162
Results of Chemical Analyses	164
White Liquor	164
Cooking Liquors	167
Trace Elements	173

Organic Species	177
Summary	178
Electrochemical Behavior in Cooking Liquors	178
Rest Potentials	178
Polarization Curves	183
Corrosion Rates	190
Ag/Ag <sub>2</sub> S Reference Electrode Calibration	190
Discussion	191
VIII. UNRESOLVED ISSUES	194
IX. REFERENCES	198
X. ACKNOWLEDGMENTS	202
XI. APPENDIX	203

# THE INSTITUTE OF PAPER CHEMISTRY

Appleton, Wisconsin

## STRESS CORROSION CRACKING OF CONTINUOUS DIGESTERS FOR KRAFT PULPING

### PREFACE

The pulping industry was suddenly introduced to a problem of serious proportions when the continuous digester vessel at the Pine Hill, Alabama, mill ruptured during routine operation in September 1980. The top of the vessel was separated from the lower vessel by failure of the weld at the bottom of the cone. Examination of this weld revealed extensive cracking of the heat-affected zone, such that the remaining ligament could no longer withstand the operating pressure. Further investigation showed that cracking had occurred in many of the girth welds in the top 55 feet of the vessel. The branched crack morphology and the preferred cracking path between grains in the metal suggested that the cracking was due to stress corrosion. The vessel required extensive repairs but was returned to service after four months.

The extent of the problem with continuous digesters was revealed as the news of the incident spread and other mills undertook careful examination of their vessels using more sophisticated nondestructive evaluation (NDE) methods. In view of the safety concerns involved, a TAPPI Task Group (TA 4561) was formed to facilitate exchange of information related to digester cracking. Earlier instances of digester cracking in the impregnation zone came to light. NDE experiences suggested that relatively deep cracks could exist, but be masked from view unless the surface was carefully prepared and then examined using wet fluorescent magnetic particle techniques. When these methods were used, it became apparent that many of the Kamyr continuous digesters had serious cracking in the welds at the impregnation zone of the digester. When cracks were

located, they were removed by grinding (or arc-air gouging and grinding) and rewelding in the field when the corrosion allowance on the wall was gone.

Reinspection of the vessels after a period of operation frequently revealed the initiation of new cracks in areas where no cracking had been previously observed, as well as cracking of the areas repaired earlier. Other remedial measures were attempted -- including stainless weld overlaying, shot peening, thermal spray coating, in situ stress relieving, and anodic protection -- with mixed results.

Faced with the prospect of continued cracking and ineffective remedial measures, the TAPPI Task Group organized industry support for a research program to investigate digester cracking and to identify effective control measures. Funds to support this program were solicited from companies whose pulp mills operated Kamyr digesters, and support was eventually received from more than eighty-five per cent of these companies. Kamyr, Inc. provided matching funds, and several related firms provided some additional funding. The representatives of sponsoring companies formed a new group -- the Digester Cracking Research Committee (DCRC) -- to monitor the progress of the research program. The Institute of Paper Chemistry agreed to administer the research program. A research subcommittee of the Task Group solicited proposals for research programs from various research agencies and, after reviewing the proposals, eventually settled on three research contractors.

Although the thrust of the TAPPI/IPC research program was to be focused on identifying effective measures to control digester cracking, the DCRC first authorized the Institute of Paper Chemistry to review and document the current state of understanding of stress corrosion cracking (SCC) in digesters. This

review was divided into three parts: (i) a review of the current understanding of SCC in alkaline sulfide media, (ii) an attempt to correlate SCC susceptibility with details of digester fabrication or operation in North America, and (iii) a chemical and electrochemical characterization of carbon steel in actual digester liquors. The effort was to provide a detailed resource document for the industry, as well as an assessment of actual digester conditions that promote cracking, with the latter assessment as a starting point for the balance of the research program. To achieve this goal, the IPC program was designed as a "crash" program to be completed by the end of 1982 -- and before the subsequent studies of remedial measures reached full stride.

Since several continuous digesters have escaped cracking after prolonged operation, an intensive effort was made to determine if some feature of these digesters differed from those at mills exhibiting marked SCC susceptibility. In an attempt to identify the reason for different SCC behavior, six mills were selected for intensive study, three of which have digesters immune to cracking and three of which have vessels exhibiting marked SCC susceptibility. None of the six vessels were stress relieved in the impregnation zone. An on-site visit was made to each mill to sample pulping liquors for chemical analysis, to conduct electrochemical studies on pressure vessel steels exposed to cooking liquors, and to delve into the details of digester fabrication and operation. By comparing data obtained at immune and susceptible mills, it was hoped that a correlation between SCC susceptibility and some aspect of digester use would be apparent. Survey questionnaires were also distributed to the rest of the mills operating Kamyr digesters, in an attempt to relate routine operation practices to cracking behavior. Information on repair method effectiveness was also gathered. The final aspect of the IPC program was a detailed literature survey

of SCC of carbon steel in alkaline media, to provide corrosion specialists on the DCRC and the contractors to the DCRC with an up-to-date review of the current understanding of SCC as it affects the DCRC program.

Since much of the information obtained from survey forms, pulp mill visits, and conversations with engineers and consultants was given in confidence, care has been taken in this report to preserve the confidentiality of this information. In general, the sources of information discussed in this report are not identified unless permission has been received or the information is already in the public domain. Since sources cannot be checked, special care has been taken to identify hearsay and other tenuous sources of information in the text.

In some cases, companies operating continuous digesters have chosen not to cooperate with the surveys conducted as part of this program. As the cracking problems came under control and concerns for safety waned, these companies have exercised their right to preserve the confidentiality of their information. The point is raised only to caution the reader about the possibility of inaccurate conclusions based on an incomplete data base.

Virtually all of the information cited in this report was obtained from mills in North America. In a few instances, data were included from mills in Europe and Australia to supplement the North American data base. These supplementary data will be clearly identified in the text.

This report is written for a variety of audiences, with some sections addressed to the nontechnical executive and others addressed to the corrosion specialist. Some sections are tutorial and are intended as background reading for those unfamiliar with stress corrosion cracking. The intended readership



and the level of detail in each section is indicated are a footnote at the start of each section.

## EXECUTIVE SUMMARY

The Institute of Paper Chemistry has completed a preliminary examination of stress corrosion cracking (SCC) in Kamyr continuous digesters. The objectives of this study were to: (i) review the current understanding of SCC in alkaline sulfide media, (ii) correlate SCC susceptibility with details of digester fabrication or operation, and (iii) characterize the liquor chemistry and electrochemistry in the vicinity of observed cracking. Chemical and electrochemical tests were conducted in actual liquors at six mill sites -- three with cracked vessels and three with immune vessels. Questionnaire responses, including detailed surveys conducted at the six selected mills, were analyzed in the search for correlations between cracking susceptibility and digester conditions. A "crash program" was instituted, with a plan to provide a final report within 120 days, so the information obtained would be available for use in the balance of the Digester Cracking Research Committee studies.

A detailed review of stress corrosion cracking in alkaline sulfide media is provided in the text, together with a tutorial introduction to the topic. Caustic cracking of carbon steels is characterized as a common occurrence requiring high stresses, intermediate caustic concentrations, and an electrochemical potential within a narrow range. The effects of metallurgical variables on cracking are relatively minor.

Large, nonstress relieved vessels were more susceptible to cracking than small, stress relieved vessels. No other correlations between cracking susceptibility and details of digester operation and fabrication were found, although many possible correlations were examined and discarded. Specifically, cracking susceptibility appears to be unrelated to the following: age of the

vessel, fabricator, metallurgy of construction materials, acid cleaning practices, average white liquor characteristics, wood species pulped, types of recovery and recausticizing systems, digester operating practices, final product, water source, and bleaching conditions.

No correlation was found between cooking liquor characteristics and SCC susceptibility. The average white liquor compositions reported by mills in their responses to questionnaires could not be related to cracking susceptibility. Similarly, analyses of raw white and make up liquor samples taken from immune and susceptible mills revealed no liquor characteristics that controlled cracking susceptibility. White liquors and make up liquors were similar at both immune and susceptible mills. However, the characteristics of cooking liquors in the impregnation zone of continuous digesters -- the actual site of cracking -- remain unknown.

Electrochemical studies of the short term behavior of carbon steels in make up liquor revealed conditions appropriate for cracking at both immune and susceptible mills. Pressure vessel steels exposed to make up liquors exhibited a slow, spontaneous passivation (i.e., protective film formation) process accompanied by a drift of the electrochemical potential into the range required for caustic cracking under laboratory conditions. Base metal and weld metal behaved similarly. Oxidation/reduction processes involving species in the make up liquor prevented further drifting, so potentials remained stable in the regime of high SCC susceptibility. However, no attempt was made in this phase of the research program to determine if the rest potentials of the vessels themselves duplicated the behavior of test coupons.

The reasons for immunity to SCC at certain mills remain unknown. The electrochemical conditions for cracking appear to be satisfied for short term

tests. However, other conditions for cracking -- high tensile stress, access of the electrolyte to the metal, etc. -- may remain unsatisfied in immune vessels.

Remedial measures of various types have been employed in digesters. The most durable measure in current use is weld overlaying of affected welds with stainless alloys. Shot peening, plasma spray coating, anodic protection, and in situ stress relieving are all under active study, but results are too limited to judge the long-term effectiveness of these measures.

AN INTRODUCTION  
TO  
STRESS CORROSION CRACKING\*

Stress corrosion cracking (SCC) is a term describing the initiation and growth of a crack in a susceptible metal due to the simultaneous action of a static (or nearly static) tensile stress and an aggressive environment. As shown schematically in Fig. 1, all three components -- stress, environment, and a susceptible alloy -- must be simultaneously present for stress corrosion cracking to occur. Removal of one of these components, e.g., stress, will prevent the initiation of a crack or the continued growth of an existing crack. For reasons discussed later, stress corrosion will not occur when an alloy is alternately exposed to stress and an appropriate environment.

For many years it was thought that an alloy would exhibit SCC in only a few specific environments. For example, copper alloys were notoriously prone to SCC in environments containing ammonia, but showed little cracking tendency in environments containing chlorides. Aluminum alloys seemed immune to cracking in ammoniacal solutions, but showed remarkable susceptibility to chloride-induced SCC. Pure metals seemed immune to any form of SCC. Unfortunately, the list of specific environments causing SCC grew discouragingly long as more and more environments were found to cause cracking in each alloy. It is now recognized that, while many environments may not cause SCC, there are many that will induce SCC in most alloys.

At first, it may seem unusual that the most aggressive environments from the corrosion standpoint are generally not the most potent environments for

---

\*An introduction to the topic for the nonspecialist.

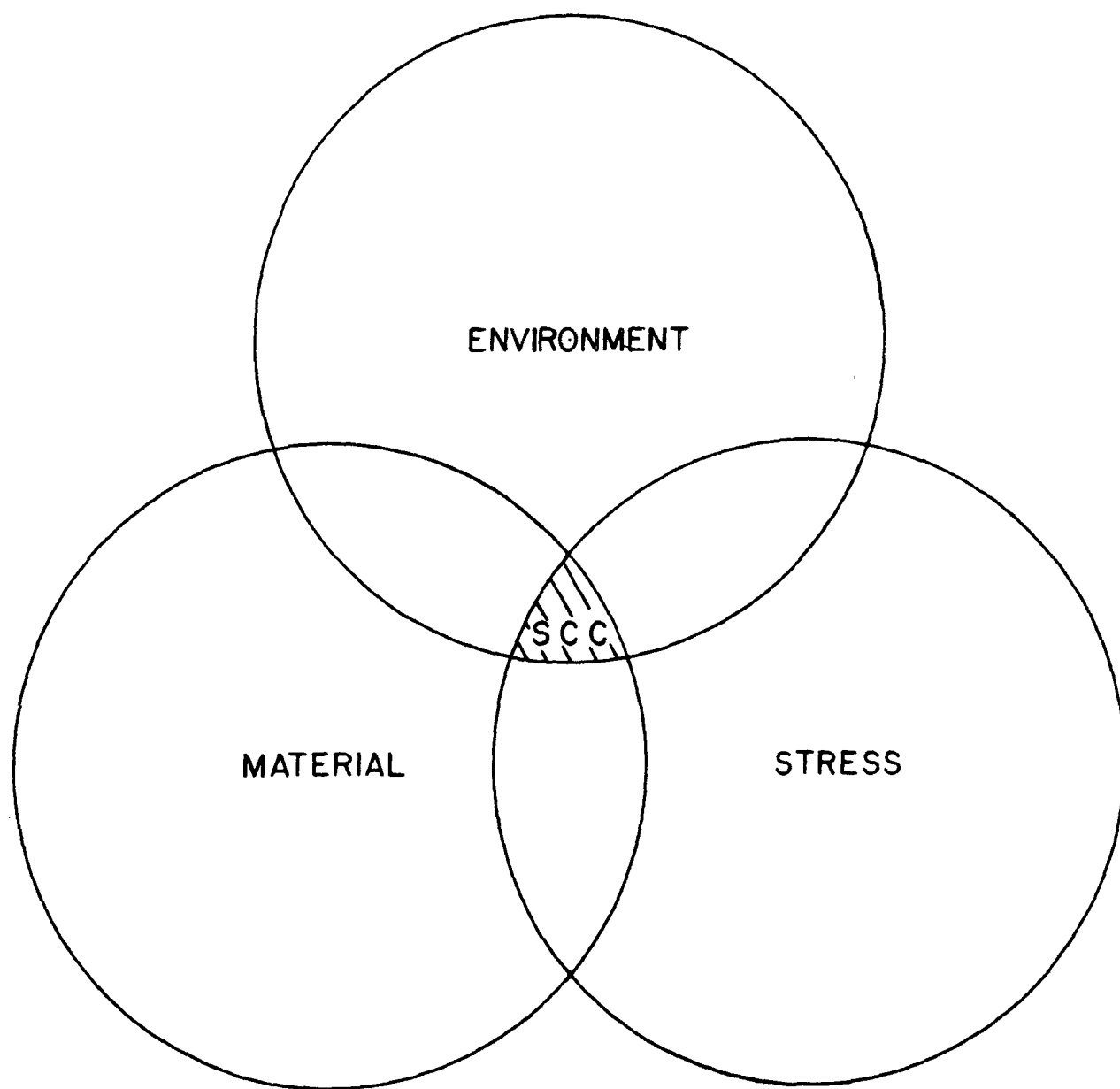


Figure 1. SCC cracking occurs only when the stress, environmental solution, and the metal combine to cause a susceptible condition.

crack growth. Those environments that are capable of high rates of metal removal by corrosion are equally capable of dissolving and removing incipient cracks or blunting cracks by dissolution at their crack tips. In effect, the rate of general dissolution in very aggressive media is greater than the rate of growth of a crack.

The alloy/environment combinations which are most likely to cause stress corrosion cracking are those which are capable of establishing a protective film on the metal surface. A metal with such a film is said to be passive, since the film prevents continued dissolution of the metal. Metals which are freely corroding in the absence of a protective film are said to be active. Every film formed during corrosion is not necessarily a passive film, since many corrosion products do not form the tight, adherent films required for protection. Rust, for example, is a diffuse precipitate of corrosion products that offers little protection for the underlying iron. When iron is alloyed with chromium in sufficient quantities, however, the surface is protected by a very thin protective film of chromium-rich oxide, and the alloy is "stainless" in many environments.

With some alloy/environment combinations, a metal may be either active or passive. In some cases, a metal may initially be active -- i.e., freely corroding -- when immersed in the solution, but gradually become passive as a protective film forms. The change from active to passive corrosion behavior is called the active-passive transition. When alloys are capable of an active-passive transition in a given environment, the alloy/environment combination is usually one which causes SCC. The reason is shown in simplified fashion in Fig. 2. Most of the alloy surface is passive since it is covered by a protective

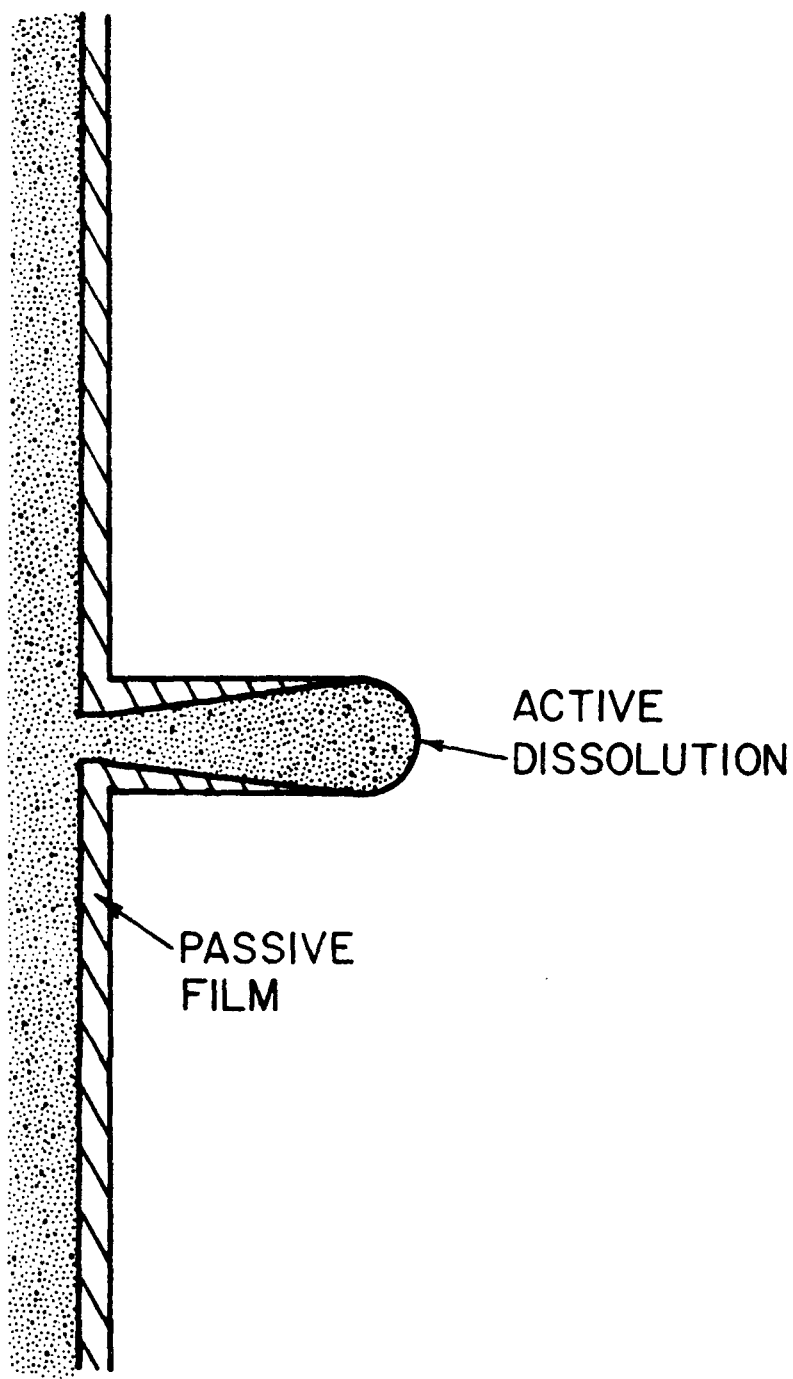


Figure 2. Cracking in active-passive media occurs when active dissolution occurs only at the crack tip, while the rest of the material is covered with a protective passive film.



film; dissolution and cracklike behavior are only observed at the isolated active sites.

The role of the tensile stress is to cause plastic deformation at the tip of the growing crack; this ruptures the protective film and permits renewed corrosion at the crack tip. The presence of the crack causes a concentration of the tensile stress at the tip of the crack, as shown in Fig. 3. The yield strength of the metal can be exceeded at the crack tip, and a time-dependent deformation can occur thereafter. The film formed on this slowly deforming substrate is more brittle than the metal and cannot accommodate the same strain as the metal without rupturing. When the film ruptures, bare metal is once again exposed to the solution in the crack, and a renewed dissolution occurs there. The film re-forms slowly, and the whole process can occur repetitively.

The process of crack growth can be visualized in several different ways, depending on the alloy, the environment, and the corrosion behavior. In the simplest case, called the slip dissolution growth model, the crack grows by preferential dissolution of metal at the crack tip. In a second growth model, called the film-rupture mechanism, the protective surface film itself is thought to rupture, followed by another and yet another film formation and rupture event. In a third mechanism, hydrogen liberated by the corrosion process migrates in the metal to the tip of the crack and induces a localized embrittlement event there. The last model assumes the presence of a specific ion that adsorbs on the metal surface at the crack tip and weakens the atom-atom bond, thereby causing separation of atom planes. Each of the models described above is supported by experimental evidence in at least some instances, but the slip-dissolution and hydrogen embrittlement models are most general.

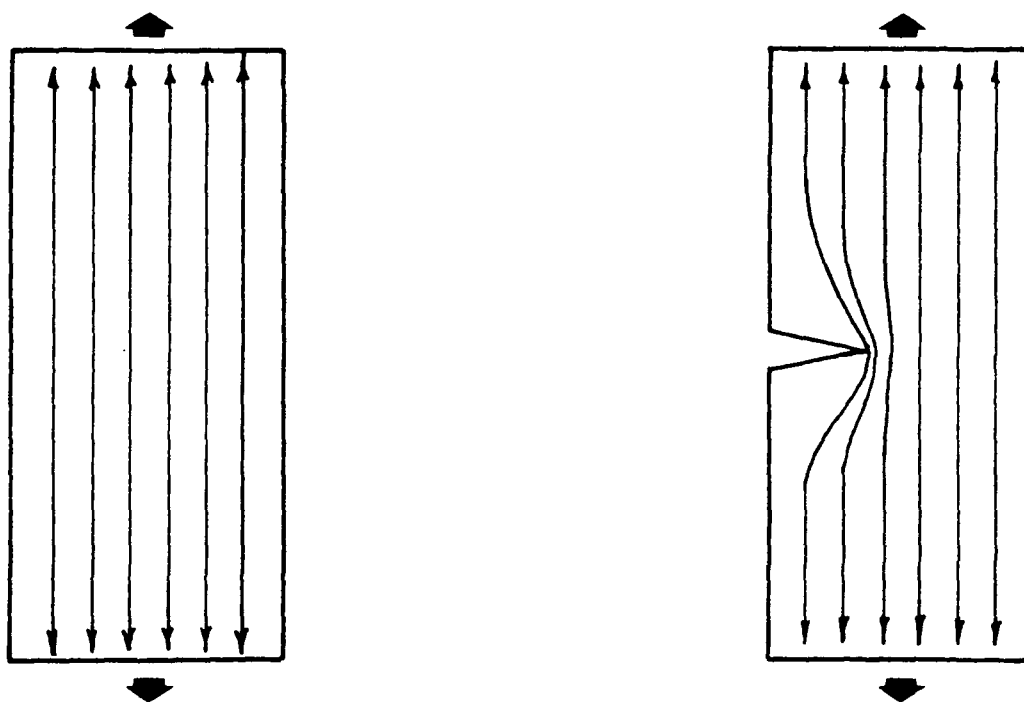


Figure 3. Tensile stresses are concentrated at the tip of a crack, thereby facilitating film rupture and renewed dissolution there.

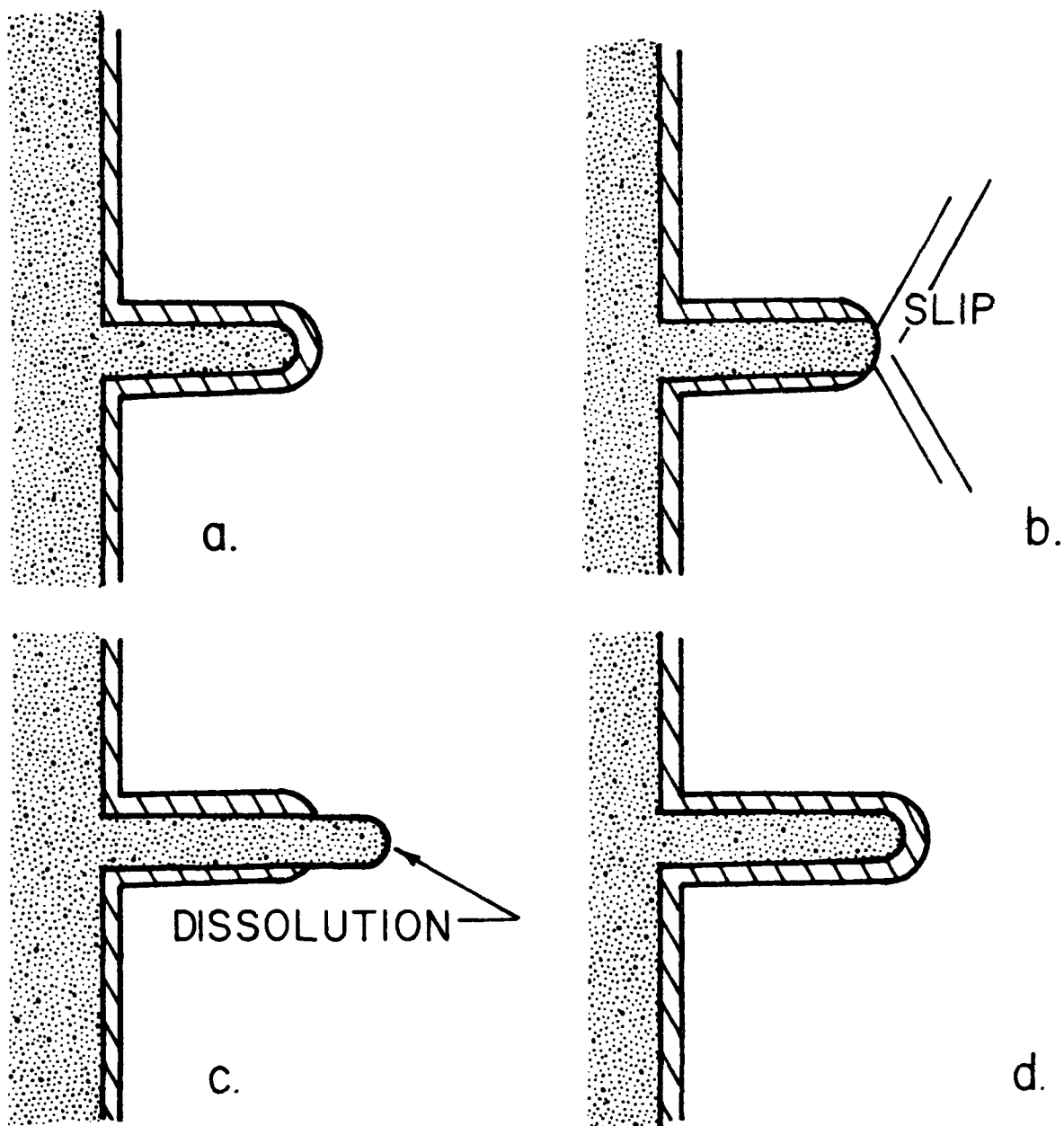


Figure 4. Schematic drawing of the slip-dissolution model for SCC.

The sequence of events in the slip dissolution process of cracking is shown schematically in Fig. 4. The applied stress causes localized plasticity at the tip of the crack, which ruptures the film and allows renewed dissolution at the crack tip. Gradually, the bare metal passes from the active to the passive stage as the exposed metal becomes covered with a new protective film. The crack does not blunt out -- the stress concentration would be reduced if it did blunt -- because of the more rapid repassivation of the sides of the crack. The full force of the corrosion penetration is focused on the crack tip region. After the film is restored, no additional growth occurs until the strains in the metal at the crack tip are large enough to rupture the film and initiate another dissolution event. The crack grows by a repetition of these deformation/dissolution events. In this model, the importance of the active/passive behavior of the metal in the solution is obvious.

The hydrogen embrittlement scenario is shown schematically in Fig. 5. Hydrogen is sometimes evolved in the crack tip region as a part of the corrosion process; for example, hydrogen bubbles are formed when metals dissolve in concentrated acids. Some of the hydrogen evolved can enter the metal and diffuse toward areas of high stress. The crack tip is a region of very high stress due to the stress concentration caused by the discontinuity in the metal, and the metal at the crack tip is thereby enriched in hydrogen. For some metals, the presence of dissolved hydrogen in the metal lattice can cause embrittlement, i.e., an inability to accommodate plastic deformation without fracturing. When a region at the crack tip is enriched in hydrogen, the concentrated stresses rupture the enriched area, and the crack is incrementally advanced. The whole process of hydrogen absorption and migration starts over again, and the crack grows another increment when the stress and the hydrogen concentration are both high enough to cause localized fracture by hydrogen embrittlement.

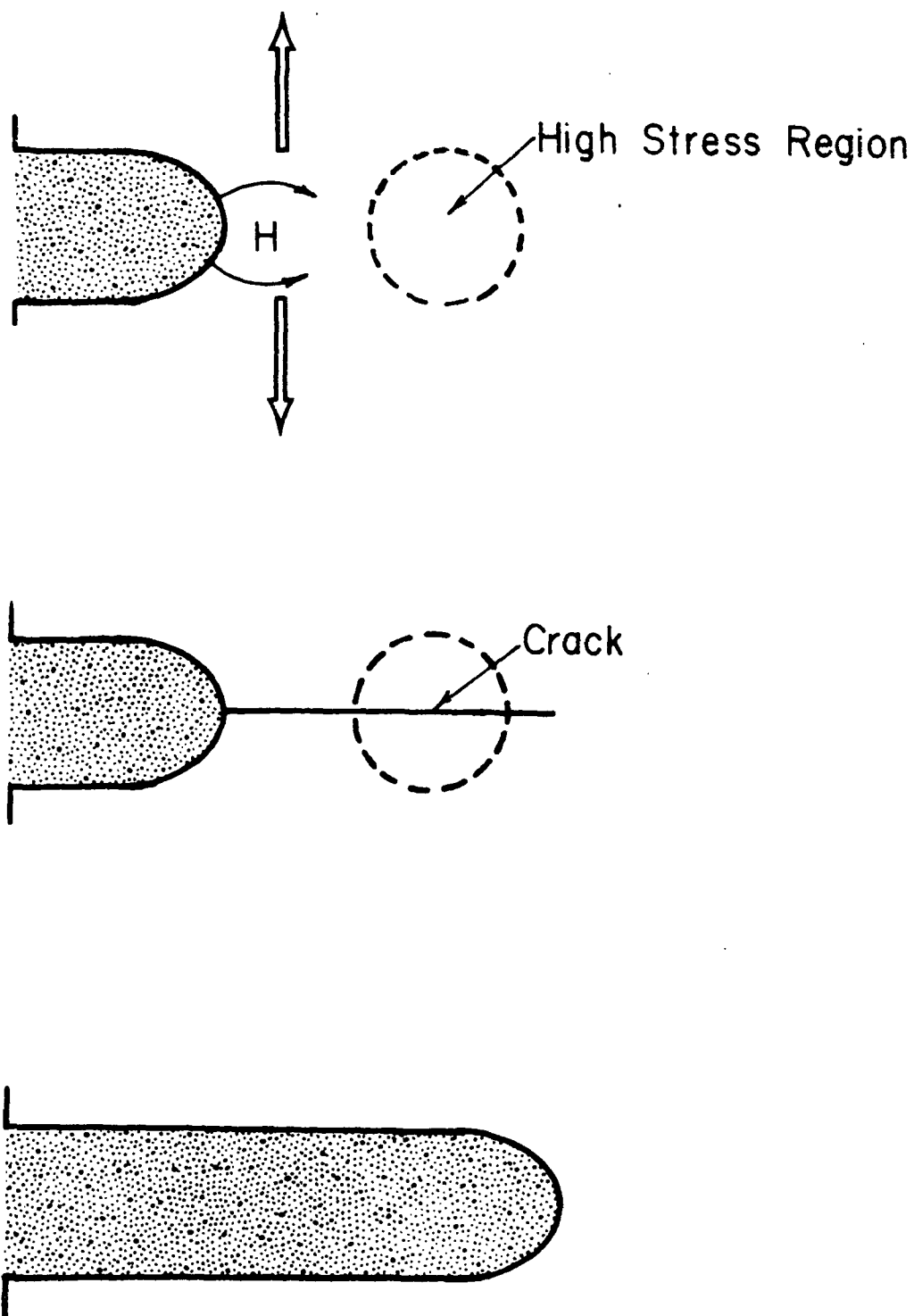


Figure 5. Schematic drawing of events causing SCC via the hydrogen embrittlement model.

The film rupture model shown in Fig. 6 is thought to occur when the film formed on the surface of a metal exposed to the environment is thick and brittle. In this case, the crack tip is covered with the film, which is then ruptured by the crack tip stresses. The crack tip is then exposed to the solution and the thick film re-forms and is again ruptured, causing incremental advances in the crack front. The process is similar to that occurring in the slip dissolution model, except that the crack advances by rupturing the thick film, rather than by active dissolution.

The specific adsorption model is shown schematically in Fig. 7. In this case, a specific ion migrates down the narrow groove of the crack and adsorbs on the metal surface in the highly stressed region of the crack tip. The ion interferes with the normal bonding between atoms, and the cohesion of the metal is lost when the atom-atom bond ruptures. The crack grows by an atom spacing increment every time a specific adsorption event takes place.

For iron-base alloys, SCC is usually thought to occur either by hydrogen embrittlement or by slip-dissolution processes. Steels and other iron-base alloys generally do not form the type of film required for growth by the film rupture mechanism in environments known to cause cracking -- hydroxide, carbonate, nitrate, and sulfide media. The specific adsorption process may be occurring, but it is a difficult process to verify because of the localized nature of the damage process. The hydrogen embrittlement model is most appropriate for high-strength steels, since lower-strength steels normally deform instead of developing the high stresses required for fracture in the presence of hydrogen.

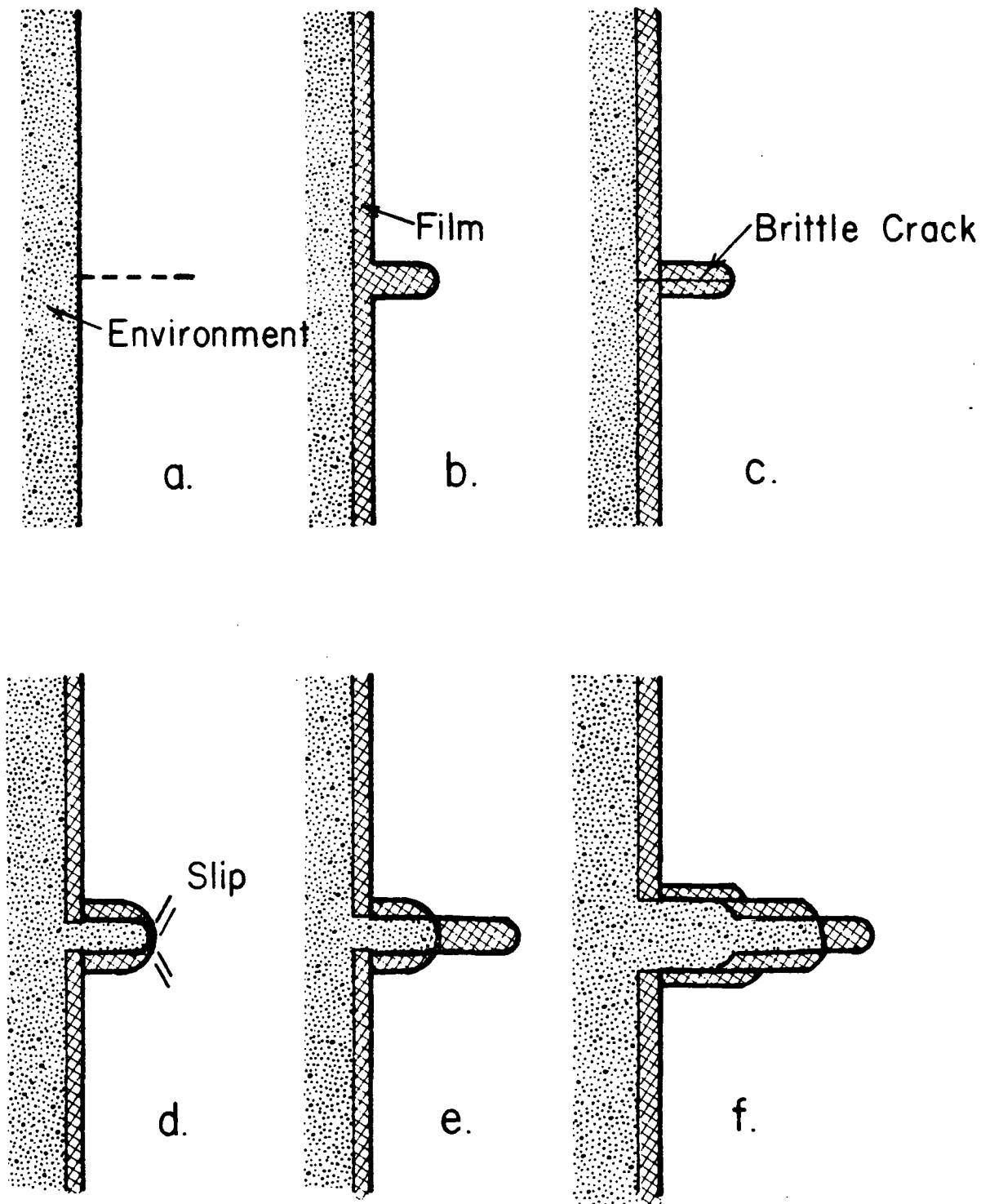


Figure 6. Schematic drawing of events causing cracking by the film rupture process.

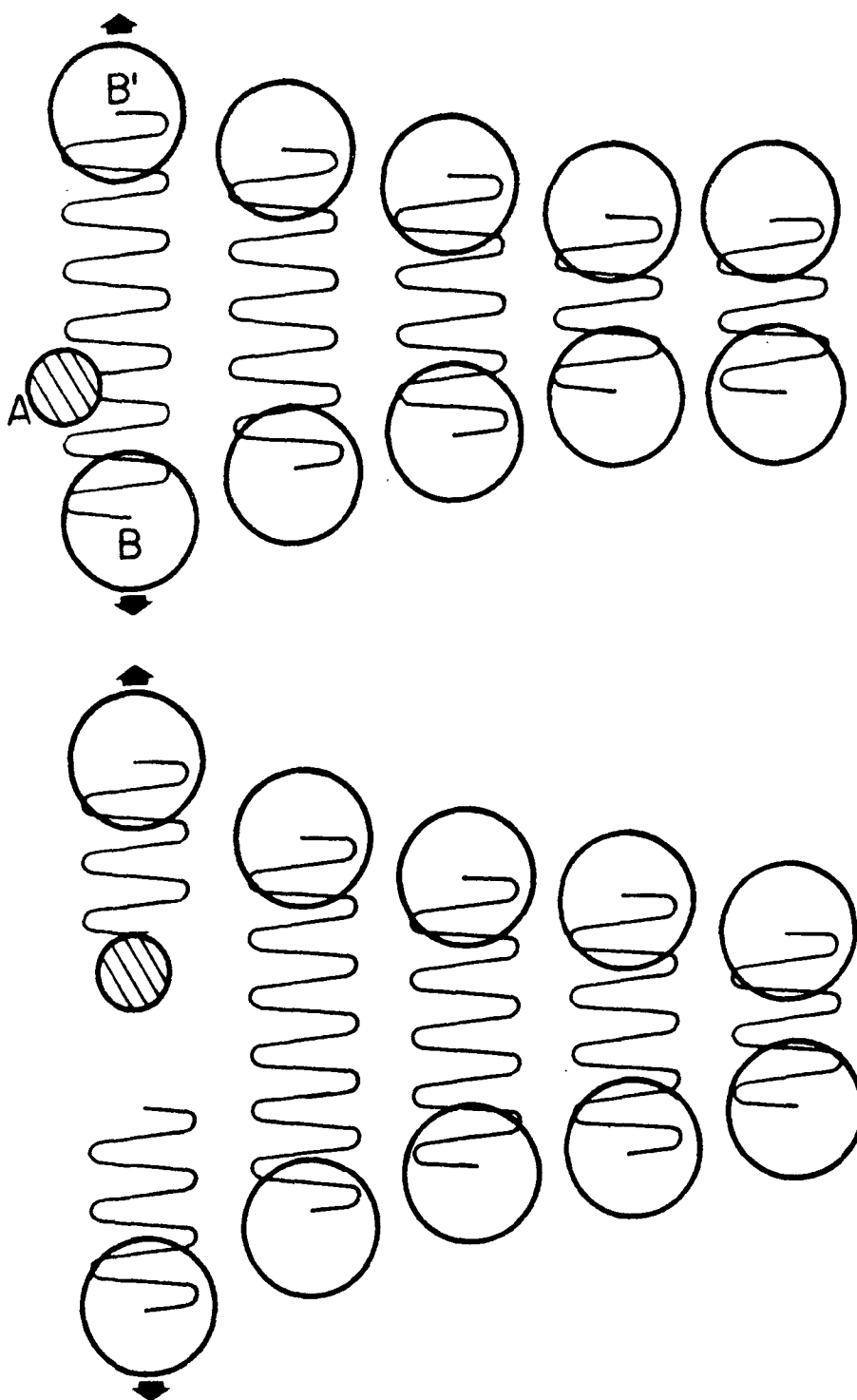


Figure 7. Crack advance by adsorption of an ion, A, causing breakage of atomic bonds between B-B<sup>1</sup>, causing crack growth.



### Crack Path

In some cases, a stress corrosion crack follows some microstructural feature of the affected metal, whereas in other cases, the crack seems to follow the plane that experiences the highest tensile stress normal to it. A common crack path in SCC is in the region between the individual grains that exist in metals. Grains are microscopic crystals of metal with different orientations, and the boundary between these grains is often particularly susceptible to cracking because it has a composition that differs from that of the bulk metal. In this case, the crack path is said to be intergranular. When the crack path cuts across the grains, the path is said to be transgranular. Often, the crack will grow with both intergranular and transgranular paths.

### Stress

A tensile stress is necessary to induce crack advance in stress corrosion cracking. Compressive stresses do not tend to open up cracks and permit access of electrolyte to the crack tip, nor will they provide the forces necessary for the hydrogen-assisted crack growth.

Stresses required for crack initiation and growth can be different because of stress concentration effects. For smooth specimens, the nominal applied stress often must be high enough to cause localized yielding at some area on the surface of the metal. In other cases, nominal stresses well below the yield strength of the alloy will permit initiation of stress corrosion cracks. At present, it is not possible to predict the nominal applied stress below which cracking will not occur, although such a threshold stress can usually be demonstrated empirically.

The presence of a crack, notch, or other surface flaw can dramatically reduce the nominal stress required for crack growth. The rate of crack growth

is usually related to applied stress intensity, rather than applied stress. The stress intensity is usually expressed as a product of the applied nominal stress, an expression containing the crack length, and a third expression that depends on the exact geometry of the cracking situation. For example, for a single edge crack of length  $a$ , subject to a nominal stress ( $S$ ), the stress intensity ( $K$ ) is given by

$$K = S\sqrt{a} \cdot (1.1 \sqrt{\pi}) \quad (1)$$

Based on stress intensity expressions such as that given above, the same driving force for crack growth can be obtained with a high stress and a short crack, or a low stress and a long, deep crack. The same rate of growth is expected at a given stress intensity level, regardless of the contributions to  $K$  from the three terms in Eq. (1).

When SCC growth rates are measured as a function of stress intensity, three stages of growth are usually encountered, as shown in Fig. 8. At low stress intensities (Stage I), the logarithm of the crack velocity is proportional to stress intensity. At some value of  $K$ , the crack velocity is constant and independent of the stress intensity (Stage II). At still higher stress intensities, the crack velocity increases again, until final overload velocities occur. There exists a threshold stress intensity,  $K_{ISCC}$  below which crack growth rates are so low ( $10^{-10}$  m/sec) that no significant damage occurs in achievable time frames.

When stress corrosion cracks grow, the stress intensity can increase or decrease, depending on the relative changes in the load and crack length terms in Eq. (1). If the stress is held constant, as is the case for pressure stresses

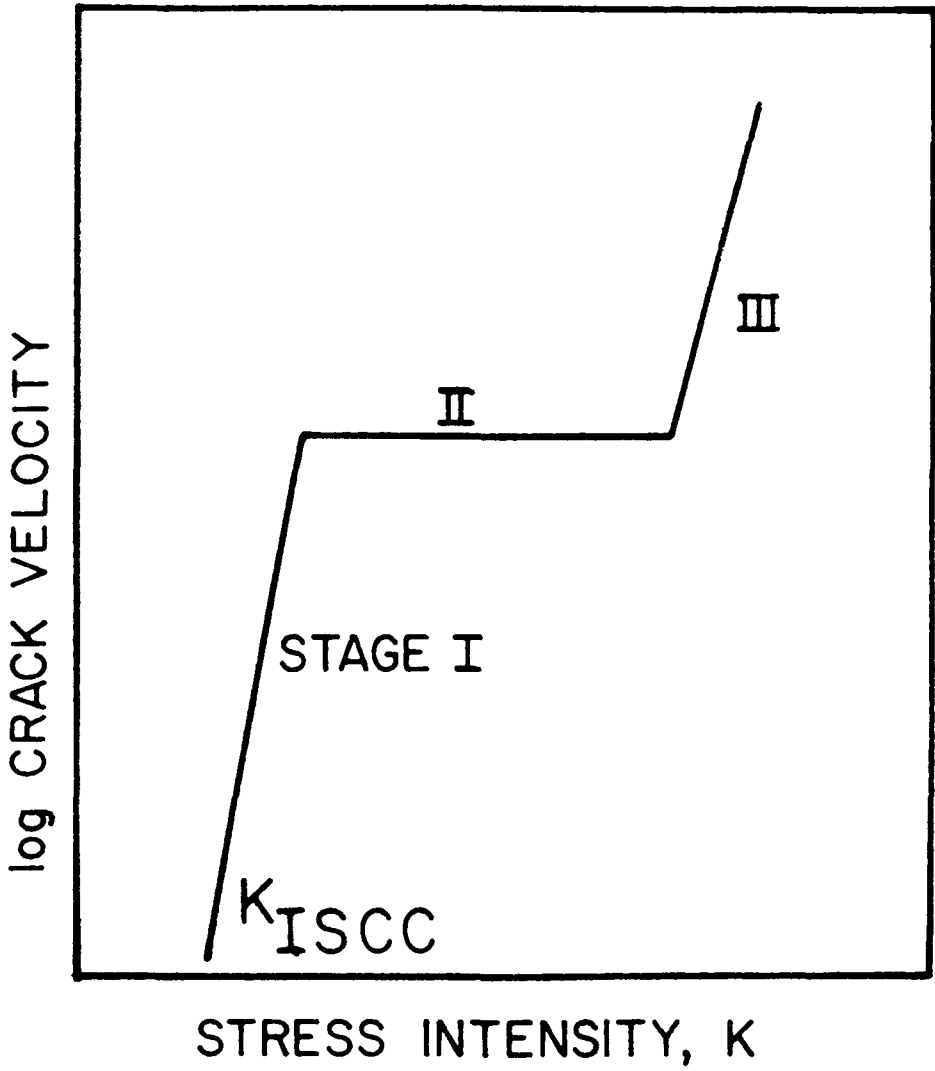


Figure 8. Typical three-stage growth of cracks in SCC.

in a thick-wall vessel for example, the stress intensity increases as the crack lengthens. If, on the other hand, the stresses arise from a constant deflection condition such as differential thermal expansion, the stress will likely decrease faster than the crack length term increases, and the net stress intensity decreases as the crack grows.

Stresses large enough to cause stress corrosion cracking can arise in several different ways. The most obvious stresses are structural stresses associated with containment of pressure or structural stability. Stresses can also arise from mismatch of mating parts during fit-up in fabrication, or as a consequence of welding without a subsequent stress relief treatment. These latter stresses are always present, even during periods when direct stresses are missing, and they are therefore called residual stresses. Another source of applied stress is differential thermal expansion of structures or components during operation. All of the direct stresses can fluctuate periodically during routine operation, and there is some evidence that these periodic changes can enhance crack initiation and growth.

#### Temperature

Since corrosion is a thermally activated process, it is not surprising to find that increases in temperature can exacerbate stress corrosion cracking. This acceleration of cracking is probably due to enhanced dissolution at the crack tip (in the slip-dissolution process) or enhanced hydrogen mobility (in the hydrogen embrittlement model). The temperature may also influence the propensity of the metal to reside in the active-passive transition region.

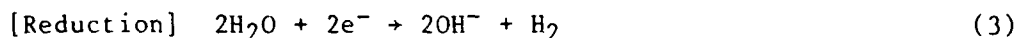
#### Potential

Every metal immersed in an electrolyte exhibits a voltage gradient in the vicinity of the metal-liquid interface, and this potential has a profound

effect on the SCC behavior. The magnitude and sign of the voltage are determined by the nature of the oxidation (i.e., corrosion) and reduction reactions that occur on the metal surface. Two or more reactions occur at the metal-electrolyte interface. When metal atoms go into the electrolyte as ions, they leave behind electrons as in the reaction . . .



The electrons thus created must be consumed by some reaction at the metal surface, or the dissolution reaction will soon stop. A common reaction that consumes electrons is the hydrogen evolution reaction, which occurs at high pH by reaction . . .



The voltage (or potential) at the metal-electrolyte interface is that voltage where all of the electrons created by oxidation are consumed by reduction processes. The potential at which this occurs is called the open circuit corrosion potential,  $E_{\text{corr}}$ .

As shown in Fig. 9, the sign and magnitude of  $E_{\text{corr}}$  are determined by measurements made with a high resistance voltmeter and another electrode immersed in the solution -- the reference electrode. Reference electrodes are electrodes that always have the same value of  $E_{\text{corr}}$  and consequently can be used as reference points in the measurement of unknown voltages. By universal agreement, the zero voltage point is the  $E_{\text{corr}}$  where the only oxidation and reduction reactions involve hydrogen. This reference electrode is called the standard hydrogen electrode, S.H.E. Since hydrogen electrodes are difficult to work with, most routine measurements are made with reference electrodes whose constant potential is known versus the S.H.E. Two common reference electrodes used are the saturated calomel electrode (SCE) and the silver/silver chloride

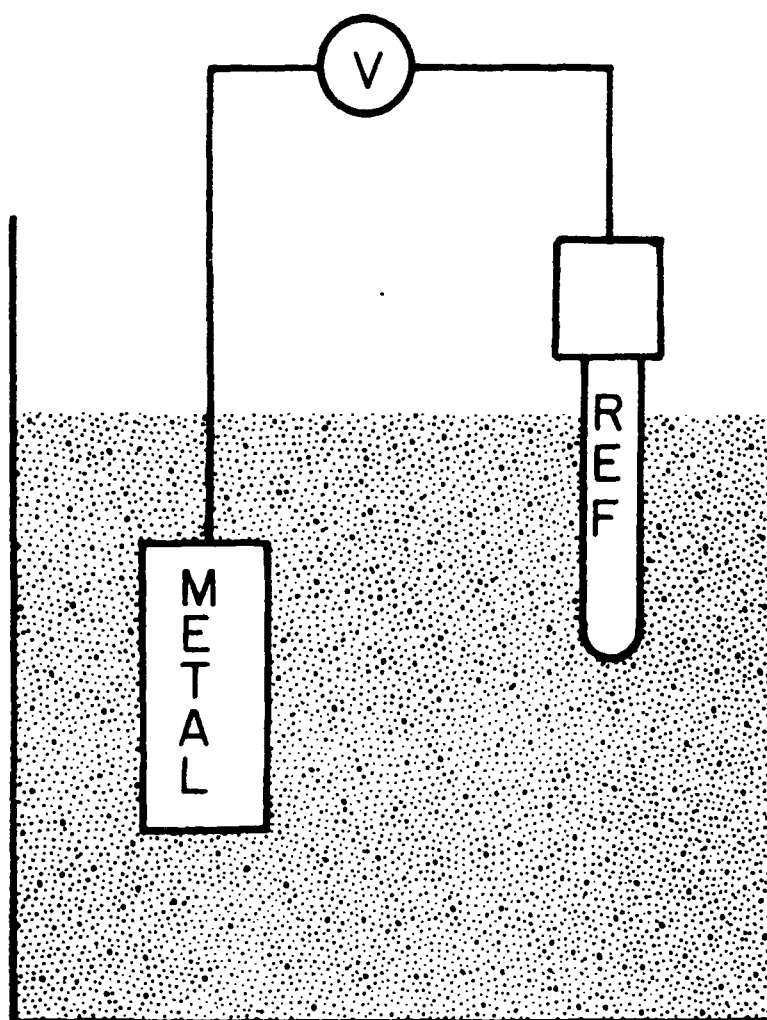


Figure 9. Measuring potentials at the metal-electrolyte interface.

adjusting the concentration of oxidizing species in the solution; these changes could be followed by monitoring changes in  $E_{\text{corr}}$ .

It is often convenient to study the behavior of metals in electrolytes by artificially biasing the balance between oxidation and reduction to maintain a potential other than the normal  $E_{\text{corr}}$ . This can be done by connecting the specimen to a source (or sink) for electrons to lower (or raise) the potential at the metal surface. The positive terminal of a battery is a good sink for electrons, and connecting the metal surface to a battery as shown in Fig. 10 will raise the potential. Conversely, connecting the metal to the negative terminal will lower the potential. By choosing the voltage and polarity of the battery, any potential can be imposed on the surface. The current that flows to or from the battery is measured via the ammeter A in Fig. 10.

In practice, an electronic potentiostat is used in place of the batteries described above. With the potentiostat, a reasonable potential can be imposed on a metal surface by a simple programming adjustment. Thus, potentials other than  $E_{\text{corr}}$  can be imposed on the metal surface to examine what the behavior of the surface would be if  $E_{\text{corr}}$  had been allowed to drift to the imposed potential. Similarly, the rate of corrosion can be accelerated or decelerated by selecting higher or lower potentials, and this is the basis for cathodic protection. If a protective film can form, an artificial potential can be chosen that will establish this passive film more quickly than would normally occur, and this is the basis for anodic protection. Finally, a potential in the middle of the active-passive transition can be artificially imposed on a test specimen to examine the SCC behavior of the metal.

By monitoring the potential versus current during gradual increases or decreases in potential, it is possible to determine whether a metal is active,

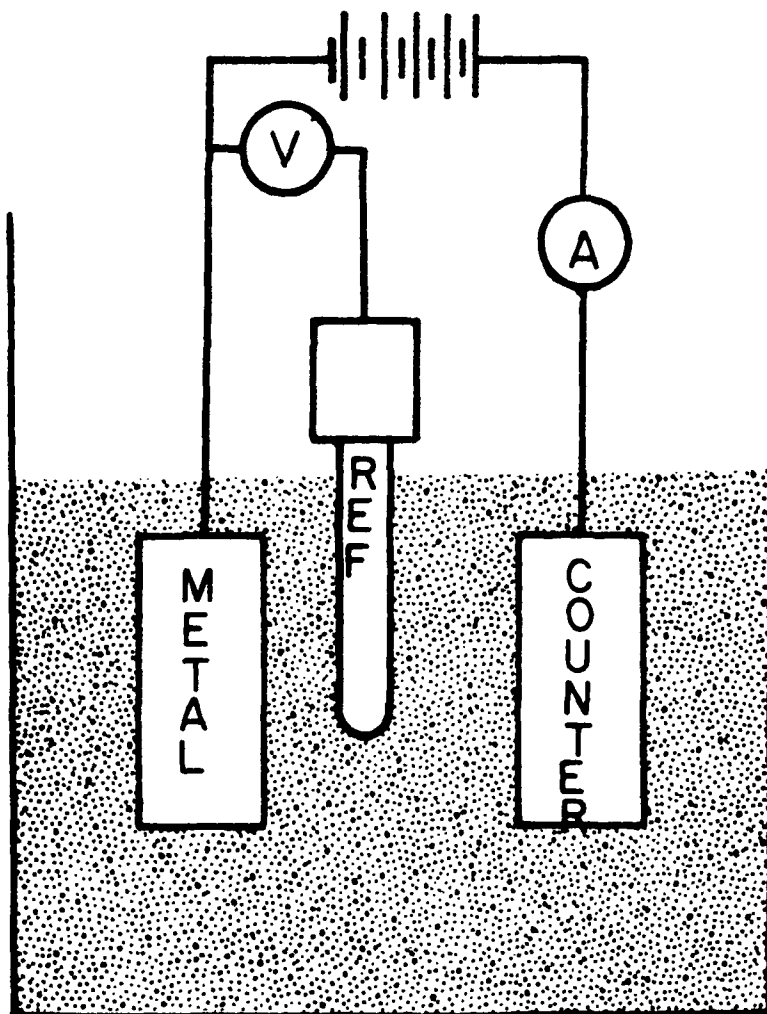


Figure 10. Imposing artificial potentials at metal-electrolyte interfaces using a battery (or potentiostat) and a counter electrode.



passive, or active/passive. A plot of potential versus (logarithmic) current is called a polarization curve, and several schematic polarization curves are shown in Fig. 11. (For convenience, forward currents and reverse currents are shown on the same figure). For an active metal, the corrosion current continues to increase logarithmically as the potential is artificially increased above  $E_{\text{corr}}$ . For a passive metal, the potential can be raised without an increase in the applied current. An active-passive metal is initially actively corroding, but when a certain potential is reached, the passive film begins to form and the applied current that can be passed through this film drops.

For an active-passive metal/environment combination, the zone where the transition occurs is the range of potential where stress corrosion cracking is particularly severe. The polarization curve helps to define if an active-passive transition will occur for a given metal/environment combination, and over what range of potentials SCC is likely. The danger zones for SCC are indicated in Fig. 12. The polarization curve is a powerful tool for characterizing SCC propensity, based on the active-passive behavior.

#### Incubation Time

Frequently, a lengthy incubation time will elapse before a metal immersed in a cracking environment will begin to show signs of crack initiation. Incubation times of 40,000 hours have been observed in lengthy laboratory tests. The processes occurring during this incubation time are not well understood. In some cases, time is required for the development of a local electrolyte that can cause cracking through some corrosion process or the accumulation of deposits on the metal surface. Corrosion pits are frequently implicated as SCC initiators because the liquid within the pits is usually much more aggressive than the

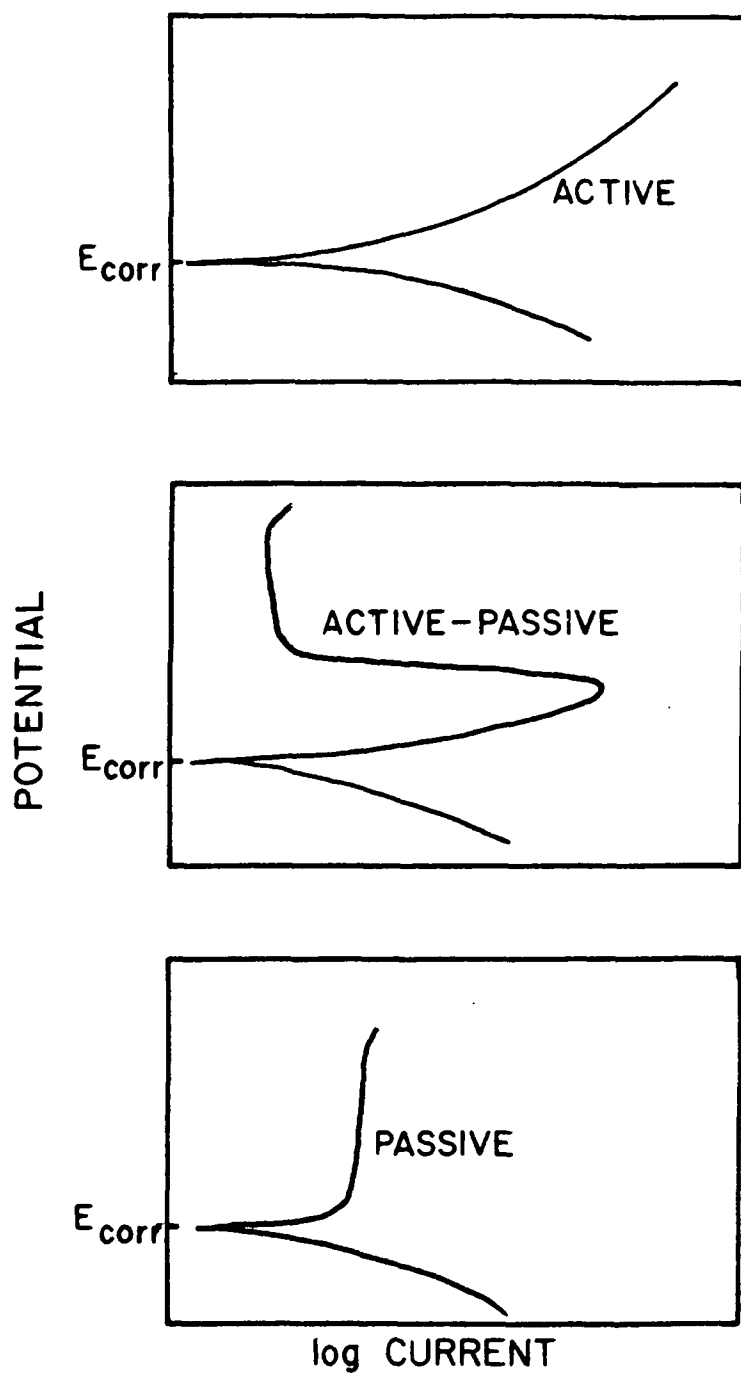


Figure 11. Polarization curves showing active, active-passive, and passive behavior.

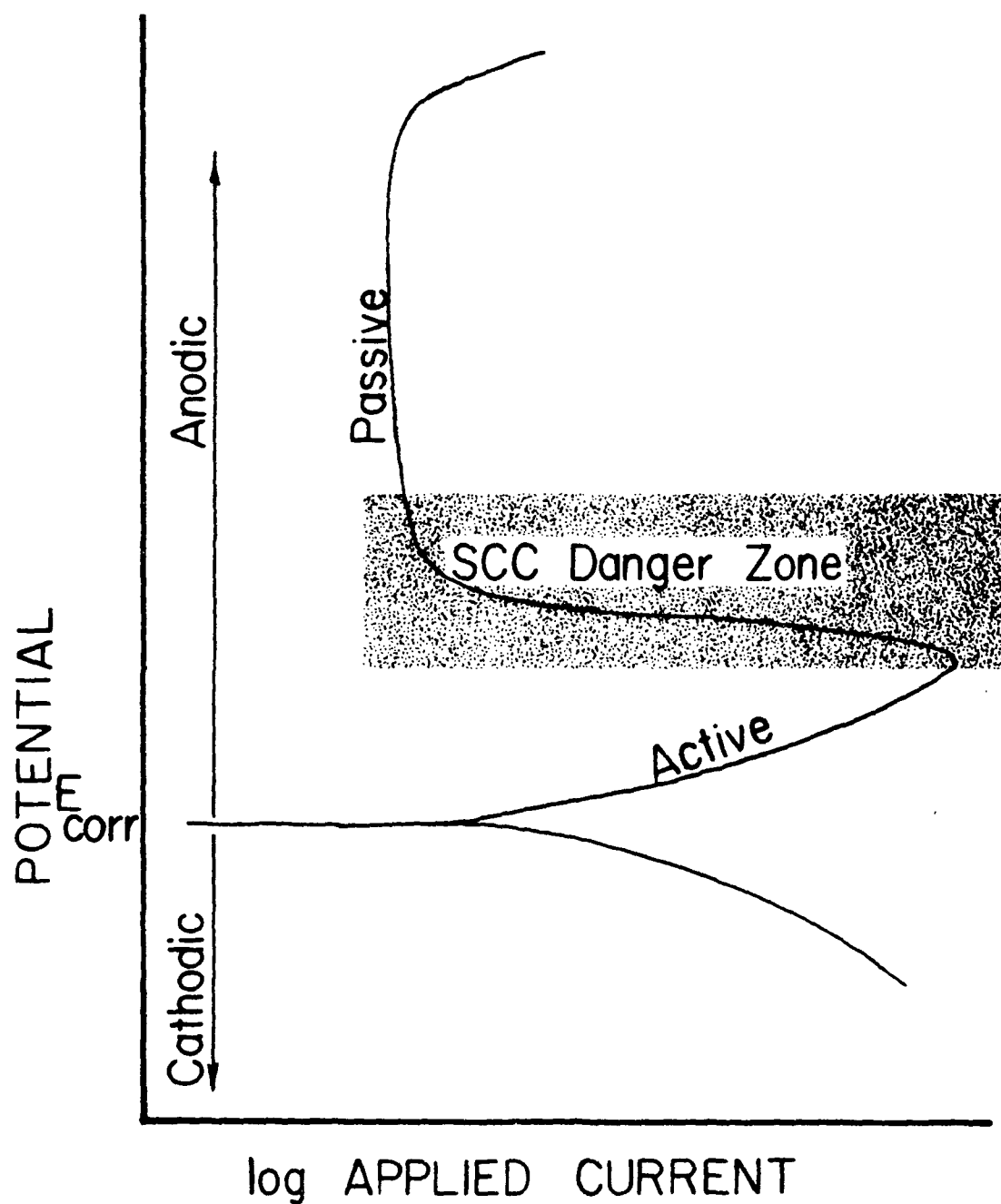


Figure 12. Danger zones for caustic cracking under active-passive conditions.

bulk liquid. Similarly, unique environments can develop under sediments or corrosion products and cause cracking after a period of apparent incubation. Passive films also exhibit "aging" behavior, and the incubation period may be the time required to age a film to the right conditions for cracking. A final interpretation of incubation times in service experience is that the nature of the environment can change during operation, and crack growth only starts when the changes bring a specific electrolyte into contact with the metal surface. Regardless of the origins, an incubation period is frequently observed before cracks initiate in laboratory and service conditions.

#### Testing for SCC Behavior

Many test methods have been used to characterize stress corrosion cracking susceptibility in metals, ranging from simple exposure of self-stressed coupons to complex slow extension rate tests (SERT) at controlled potentials. Since stress corrosion frequently takes years to develop in service, most SCC tests use some technique to accelerate the onset of cracking. For example, the stress applied to a test coupon might be high compared with actual service stress, or the potential might be controlled to promote cracking. Selection of an accelerated test method depends on the specific information sought. Some types of SCC information that are frequently sought are:

- (i) Evidence of any susceptibility to crack initiation in the environment
- (ii) Threshold stress intensity for crack growth in a cracked specimen
- (iii) Threshold stress for crack initiation in a smooth specimen
- (iv) Crack velocity at a selected stress intensity

Different tests would be chosen to provide the different types of information.

In general, SCC testing involves one of four test methods:

- A. Prolonged exposure of self-stressed, smooth specimens (i, iii)

- B. Prolonged exposure of self-stressed, precracked specimens (ii, iv)
- C. Slow extension rate tests (SERT) on smooth tensile specimens (i, iii)
- D. Electrochemical tests (i, iii)

Types A, B, C, and D are discussed in turn below.

Perhaps the simplest test to characterize SCC in a specific environment is an exposure of a smooth, highly stressed specimen to the environment for a prolonged period, with intermittent visual examination. Many methods have been used to stress the specimen during exposure, but some methods have been used more generally. A common self-stressed specimen is the U-bend, a strip of metal bent into a "U" shape and fastened at the straight shank portions with a nut and bolt. If care is taken in the assembly (an ASTM standard, G30, is available), the stresses at the apex of the "U" are tensile and well above the yield strength. A C-ring is a similar type of smooth, self-stressed specimen which has the advantage of a simple formula that can be used to calculate stresses in the apex of the "C" (ASTM Standard Method G38). In many cases, a jig is used to load a tensile specimen or a bent beam to a known stress level.

Exposure of self-stressed specimens is an inexpensive approach toward determining the susceptibility to SCC and the threshold stress required for initiation, but the testing can be tedious when incubation times are long. Usually, no information on growth rates can be obtained from this type of specimen.

Precracked specimens are frequently used to characterize crack growth behavior because the prior existence of a sharp crack before exposure reduces the incubation time for cracking. The usual practice is to select a specimen for which the stress intensity expression is known, precrack the specimen with a small fatigue load, load the crack by spreading the crack planes with a bolt

or fixture, and then expose the self-stressed, precracked specimen to the test environment. The progress of the crack is monitored visually at intervals during the exposure, and the crack growth rate calculated based on incremental growth. Hudak and Saxena (1) have recently compiled a detailed description of the test methodology for this type of test.

When the precracked specimen is a bolt-loaded specimen such as a double cantilever beam (DCB) or a wedge-open loaded (WOL) specimen, the load falls rapidly and the stress intensity decreases as the cracks grow in the specimen. Thus, the crack grows at ever diminishing stress intensity and eventually ceases to grow at all. As discussed above, the stress intensity where growth stops is the threshold stress intensity, and this quantity can be determined by testing bolt-loaded, self-stressed specimens.

Tests with precracked, self-stressed specimens are also useful for determining the relationship between the crack velocity ( $V$ ), and the stress intensity ( $K$ ), and for determining the threshold stress intensity for crack growth ( $K_{ISCC}$ ). No information on crack initiation at smooth surfaces is obtained. The costs of specimen preparation and loading are high, and the procedures are complicated if artifacts are to be avoided. In spite of the precrack, long incubation times are often observed. In many cases, the cracks emanating from the precrack are grossly branched, in which case the stress intensity expressions are no longer valid.

SERT tests are used to obtain rapid assessment of SCC susceptibility to metal/environment combinations. The test involves comparison of cracking behavior in two tensile specimens pulled to failure -- one in an inert environment and one in the environment of interest. When a metal/environment combination

will not produce SCC, the features of the fracture surface and the characteristic ductilities of the two tensile tests (reduction in area due to necking, total elongation) will be similar. If SCC is possible, the specimen tested in the aggressive environment will exhibit multiple cracks along the length of the test specimen, and the ductility will be severely reduced. Strain rates on the order of  $10^{-5}$  to  $10^{-7}$  in/in/sec are typically used, which yields SCC information in periods ranging from a few hours to a few weeks. Because a fracture is insured in a short time, incubation effects are largely eliminated.

The success of the SERT test is based on its similarity to the microscopic processes occurring at the crack tip during SCC. The slow deformation in the tensile test simulates the deformation at the crack tip. A metal which repassivates quickly will not show evidence of excessive localized dissolution following the film rupture events induced by the slow strain process. Similarly, the specimen which is actively corroding is not significantly affected by the slow deformation since there will be no film to rupture. Only those active-passive alloy/environment combinations will reveal excessive corrosion penetration as a result of the slow tensile deformation.

SERT tests can provide a rapid qualitative assessment of SCC susceptibility, including the ranking of alloys and environments based on SCC susceptibility. However, the SERT test provides no quantitative engineering information such as allowable stress or crack velocity versus stress intensity. The SERT test is strictly qualitative. Moreover, there is some concern that the SERT test is too fast to allow the hydrogen embrittlement mechanism to operate, or for the development of localized environments in pits and other crevices.

Electrochemical methods can be used in stress corrosion studies to accelerate cracking, to clarify the processes occurring and to provide a rapid

method for screening the SCC behavior of large numbers of metal/environment combinations.

The simplest use of electrochemical methods is the imposition of a controlled potential on a SERT specimen or a self-stressed coupon during exposure. This action accelerates cracking by maintaining optimal conditions for retention of an active/passive transition on the metal surface during testing. In general, the imposition of an artificial potential using a potentiostat is thought to simulate the naturally occurring processes involving gradual film formation and changes in oxidizing species. However, it must be recognized that the ability to maintain an artificial potential at the active/passive transition in the laboratory does not insure that this same potential will occur naturally in the field; nor is there ironclad assurance that the SCC behavior in the laboratory will resemble that occurring in the field in every respect.

Polarization curves can be used to ascertain whether the metal of interest exhibits active/passive behavior in the range of potentials likely to be encountered in actual service. The ability to detect SCC susceptibility with polarization curves is considerably enhanced if slow (0.3 mV/sec) and fast (150 mV/sec) voltage scan rates are used to generate polarization curves for comparison. Parkins (2) has found that the curves generated with fast and slow scans generally overlap in the potential range where no SCC is observed in long-term tests, whereas the fast and slow scans are different in potential regimes where cracking is likely. The different SCC regimes are shown schematically in Fig. 13. If an alloy can establish a protective film as soon as a passivating potential is reached, there will be little chance for cracking by localized dissolution. On the other hand, if a film is formed slowly, the currents



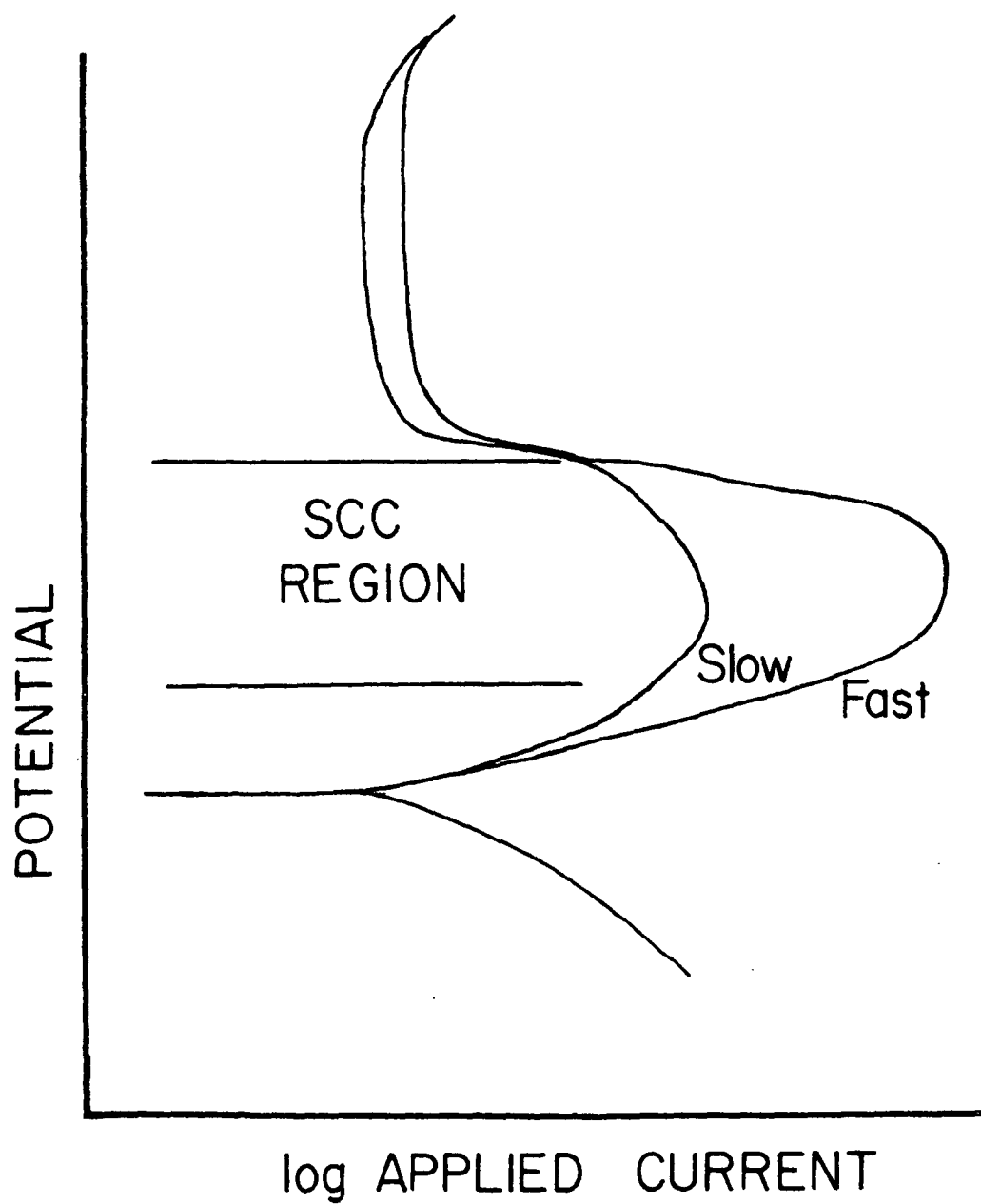


Figure 13. Regimes of cracking revealed by fast/slow scan polarization curves.

flowing in the fast and slow scan will be different, marking the likelihood of considerable crack growth whenever the passive film is ruptured at the crack tip.

The fast/slow scan technique has shown some correlation with SCC susceptibility in laboratory tests, but the test method has not yet been extensively studied. Since the method provides a very rapid assessment of SCC behavior of a metal/environment combination, the fast/slow scan method is best suited for rapidly screening SCC behavior under numerous conditions. A potential pitfall with this accelerated test method is the possibility of alternative oxidation/reduction reactions masquerading as corrosion reactions during polarization scans. If such redox reactions occur, they could exhibit fast/slow scan behavior that erroneously predicts SCC immunity or susceptibility.

In recent years, a test involving step changes in potential (from below  $E_{\text{corr}}$  to the passive regime) with measurement of the rate of current decay has been used to predict the rates of crack growth under SCC conditions. If the corrosion current falls slowly, extensive dissolution occurs and any potential cracks that form after a film rupture event will soon be neutralized by blunting at the crack tip. On the other hand, very rapid repassivation will be evident in a rapid transient in the corrosion current, and this rapid repassivation suggests that ruptured films will be restored so quickly that SCC will not occur. In the intermediate regime, where slow repassivation is indicated by a gradual reduction in the corrosion current, is the regime where SCC is indicated. Metals which exhibit intermediate current transients in a specific environment are likely candidates for SCC in that environment. The method is also relatively new, and unproven, but is so rapid that it can be used to screen

the behavior of numerous metal/environment combinations, to reduce the numbers of detailed tests such as SERT testing.

#### Remedies for SCC

The methods for controlling stress corrosion cracking usually involve removal of one of the key ingredients for SCC shown in Fig. 1 -- namely tensile stress, specific environment, or a susceptible material. The removal of one ingredient for SCC will effectively remedy the SCC problem.

Stresses can be removed or reduced in a variety of ways. A thermal treatment to reduce the built-in residual stresses is a common approach; but such treatments are usually reserved for new equipment since the high temperature treatment can have unexpected effects when the residues from prior operation are not completely removed. Tensile stresses can also be reduced by shot peening, since peening puts the first few mils of metal surfaces in a state of compression. When possible, operating stresses can be reduced by reducing pressures or decreasing loading. In some cases, alternative fabrication methods can be effective in lowering residual stresses as, for example, in temper bead welding repairs.

The environment causing SCC can either be modified by removing or altering the aggressive species, or be excluded from the affected metal by the use of coatings. In many cases SCC can be reduced by reducing contamination of the environment by aggressive chemical species. In other cases, the aggressive species are major constituents of an environment that cannot be significantly changed, and changing the environment is impractical. In these cases, coatings can be used to isolate the susceptible metal from the environment. The number of different coatings is considerable, ranging from paints to weld overlays and

thermally sprayed metal coatings. The adhesion and durability of coatings is always a concern.

Changing materials to eliminate SCC is often a good alternative when cracking occurs in small, easily replaceable components. SCC tests can usually identify superior alloys for use in any application where SCC is a problem. In the case of large, fixed pieces of equipment, the only practical materials change is the change in surface metallurgy by application of coatings, such as weld overlays and thermally sprayed coatings.

A final alternative for reduction in SCC is the installation of a cathodic or anodic protection system to maintain the potential at the metal surface outside of the SCC danger zone. Cathodic protection systems reduce the potential, whereas anodic protection systems raise the potential. In either case, an apparatus is installed to sense the potential of the metal surface and then pass a current through the metal/electrolyte interface to achieve a safe potential. Currents required for protection can be large (in some cases, impractically high) or small, depending on the conditions. Anodic protection systems can only be used in circumstances where the metal is passive or can be made passive at achievable potentials. The use of protection systems to control corrosion is a common industrial practice, but the use of these types of protection to control SCC is not well established at present.

## SCC IN ALKALINE MEDIA\*

### Introduction

There have been several excellent review articles published recently dealing with stress corrosion cracking of low-to-medium strength steels (2, 3, 4). Rather than provide an exhaustive review of these articles and the related literature, this section will focus primarily on those aspects of stress corrosion cracking which are relevant to cracking of continuous digester vessels.

The three principal constituents of kraft cooking liquors -- caustic, sulfide, and carbonate/bicarbonate -- have all been implicated in stress corrosion cracking of carbon steels under some conditions. Caustic cracking of carbon steels is a well-known phenomenon since the early studies of SCC of riveted, high-pressure boilers. Stress corrosion cracking of higher strength steels in sulfide media is also well known in the petroleum and petrochemical industries, although this form of cracking is usually associated with acidic, rather than alkaline, pH conditions. Stress corrosion cracking has also been reported in higher strength pipeline steels exposed to carbonate/bicarbonate mixtures. Stress corrosion cracking of steels also occurs in a variety of environments unrelated to kraft liquor conditions, such as nitrate solutions and anhydrous ammonia. Some of the highest strength steels may even be susceptible to cracking in relatively pure water via hydrogen embrittlement, as described in the previous section.

Since the etiology of stress corrosion cracking of continuous digesters is still uncertain, each of the three species -- caustic, sulfide, carbonate/

---

\*This section is written for the corrosion specialist.

bicarbonate -- must be considered for its potential contribution to digester cracking. Consequently, this section will begin by examining the possibilities of sulfide and carbonate/bicarbonate cracking before turning to a more thorough scrutiny of caustic cracking in sulfide media.

Although a detailed discussion of cooking liquor chemistry will be presented in a later section, some discussion of liquor chemistry in the vicinity of digester cracking is appropriate here as a basis for discussion. The overwhelming majority of digester cracks have been observed in the impregnation zone of continuous digesters, wherein cooking liquor is diffused into the chips prior to cooking. Because of the low-temperature cooking that occurs in the top circulation line, the liquor entering the top of the vessel with the chips has a caustic concentration somewhat lower than that of a typical white liquor. The liquor entering the vessel will contain approximately 40 g/L NaOH, 25-35 g/L  $\text{Na}_2\text{S}$ , 20 g/L  $\text{Na}_2\text{CO}_3$ , and a few grams per liter of the sulfoxy compounds  $\text{Na}_2\text{SO}_3$ ,  $\text{Na}_2\text{S}_2\text{O}_3$ , and  $\text{Na}_2\text{SO}_4$ . Unless polysulfide pulping is practiced, the concentration of  $\text{Na}_2\text{S}_x$  will be quite low -- on the order of a few hundred parts per million as elemental sulfur. There is also a significant organic component of the liquor due to the low-temperature cooking that occurs. As the chip slug progresses down the impregnation zone, additional low-temperature cooking takes place, which will increase the organic component of the liquor at the expense of the inorganic. The temperature of the liquor will range from approximately 200°F at the inlet to about 300°F at the top of the cooking zone.

The digester also experiences a variety of non-steady state environments that could be implicated in cracking. During start-up, for example, a batch cook is typically performed which will expose the impregnation zone to

higher than normal temperatures and perhaps higher than normal concentrations of inorganic species. During routine acid cleaning, the top portions of the vessel are usually not immersed in the acid, but they are exposed to the gaseous products of the acid cleaning process, notably hydrogen sulfide gas from the decomposition of iron sulfide films and other sulfur compounds. The role of these environmental excursions on stress corrosion cracking of digester vessels is not yet established.

The steels involved in cracking are low-to-medium strength steels containing about 0.25% carbon and silicon up to 0.35% by weight. The base metal structure is a ferrite - pearlite microstructure produced by the hot rolling (or subsequent normalizing) of the plates. The pressure vessel steels have tensile strengths in the range of 55-70 ksi, with yield strengths on the order of 35 ksi, and good ductility. A variety of weld processes are used to fabricate the vessel, but the weld metals used are all of the 70 class, i.e., chosen to develop a 70-ksi tensile strength in the weld metal.

Thus, the materials of construction and the routine environmental conditions at the site of vessel cracking are relatively well known, but the effects of nonroutine operation are unknown. The alloys involved are low-to-medium strength pearlitic steels exposed to a hot caustic solution also containing carbonate and a variety of sulfur compounds.

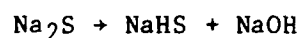
## THE POTENTIAL FOR SULFIDE CRACKING\*

Sulfide cracking is a term frequently used to denote a form of stress corrosion cracking which is promoted by the presence of hydrogen sulfide gas dissolved in the cracking media. It is generally agreed that sulfide cracking occurs as a result of a hydrogen embrittlement process involving the evolution and transport of atomic hydrogen to the tip of a crack, which grows by repeated hydrogen embrittlement events. Hydrogen sulfide appears to promote cracking by assisting in the generation of atomic hydrogen at the surface and by interfering with the formation of molecular hydrogen gas, thereby enhancing the uptake of nascent hydrogen in the vicinity of the crack tip.

Sulfide cracking susceptibility is a strong function of the pH of the sulfide environment, with a diminished SCC susceptibility at high pH. Hudgins and co-workers (5) found, for example, that the time to failure for high-strength steels exposed to a very aggressive sulfide solution increased significantly as the pH was increased above 6, with no failures at all detected when the pH was 9 or above. Dvoracek (6) found that the threshold stress for the onset of cracking of precracked specimens of high-strength steel increased as the pH increased from 3 to 8. Kahout and McGuire (7) reported that a high-strength steel would crack in a sulfide medium at a pH of 4, whereas no cracking was observed when the pH was 8.

---

\*Emphasis is placed on acid sulfide cracking; caustic cracking and sulfide cracking in alkaline sulfide media are indistinguishable. Only alkali metal sulfides have appreciable solubility in aqueous solutions, and these alkali metal sulfides hydrolyze strongly via



to form alkaline solutions.



The strong effect of pH on cracking susceptibility may be related to the ease with which hydrogen can be absorbed in a steel. Hydrogen enters steels much more readily from sulfide solutions when the pH is below 5. This may be a consequence of the effect of the hydrogen ion activity, but may also be a result of the change in the stable sulfur species as the pH increases. Pourbaix (8) reports that dissolved  $H_2S$  is stable at low pH, but is transformed into the  $HS^-$  species when the pH is about 5 ( $H_2S/HS^-$  has a  $pK = 6.7$ ). At still higher pH values, the stable species is the  $S^{=}$  ion ( $HS^-/S^{=}$  has a  $pK = 15$ ). It appears that the sulfur species must be present as  $H_2S$  in an acidic medium for significant sulfide cracking to occur.

It is debatable whether the pH of the moisture condensed on the walls of the impregnation zone during acid cleaning would fall below a pH of 8 or 9 as is required for sulfide cracking. The impregnation zone is usually not immersed in the cleaning acid, but some moisture will be present on the upper walls because of condensation. Strongly alkaline deposits are to be expected in this upper region as a residue from operation with the caustic cooking liquors, even after routine washing of the zone with water prior to acid cleaning. Since hydrogen sulfide gas evolved during acid cleaning is a very weak acid ( $pK_1 = 6.7$ ), it is unlikely to neutralize the caustic when it dissolves in the condensed moisture, even when the  $H_2S$  concentration is several thousand parts per million (as one gas analysis would indicate). The only source of an acid strong enough to acidify the condensed moisture into the cracking range is vaporized acid (typically  $HCl$ ) from the cleaning acid. Significant quantities of acid could be transported into the impregnation zone by evaporation and condensation since the cleaning acid is heated and the upper walls of the vessel will be relatively cool. However, it is unlikely that condensate from a dilute acid solution

(3-5% HCl, typically) would acidify strongly alkaline deposits in the upper portions of the vessel. If the moisture condensed on the walls was acidified into the cracking regime, most cracking should be expected adjacent to the upper cooking screens where acidification would be highest, yet there seems to be no such correlation (see later sections). Thus, it seems unlikely that the acid cleaning process could lower the pH sufficiently to induce sulfide cracking in the impregnation regions of the vessel.

A more compelling argument against sulfide cracking of digester vessels during acid cleaning is the observation of very limited cracking in the low-to-medium strength steels and weld metals used in continuous digester vessels. In an acidified chloride solution saturated with  $H_2S$  gas at  $pH = 3.8$ , the threshold stress for cracking of smooth specimens was above the yield strength for all quenched and tempered steels whose yield strength was above 85 ksi (9). For a normalized steel, stresses just below the yield strength were required to obtain cracking in 21 days in this very aggressive environment. In another study (10), the threshold stress intensities for crack growth in precracked specimens exposed to acidified,  $H_2S$ -saturated environments increased with decreasing strength of the steel. Although no steels were examined whose yield strengths were below 60 ksi, these medium-strength steels required a stress intensity of 25 to 45 ksi  $\sqrt{in}$  for crack growth in a very aggressive medium. An approximate fracture mechanics calculation shows that a tensile stress above 70 ksi (i.e., much greater than the yield strength) would be required to propagate a 1/8"-deep crack in this acidified,  $H_2S$ -saturated solution. For comparison, a 1/8"-deep crack in a steel with a yield strength of 180 ksi would grow when the stress was only 22 ksi.

The National Association of Corrosion Engineers (NACE) recommends the use of steels with hardness below  $R_c$  22 for  $H_2S$  service. These steels include

hot rolled carbon steel similar to the pressure vessel steels used in digesters. The  $R_C$  22 hardness corresponds to a tensile strength of about 110 ksi. Thus, all of the steels used in digester vessel construction should be resistant to sulfide cracking according to the NACE criteria. Several authors have verified the resistance of low-strength carbon steels to sulfide cracking. Ishizuka and Onishi (11) verified that two mild steels with yield strengths near 40 ksi were immune to sulfide cracking in a very aggressive environment, even though they were loaded to the yield strength. Bates (12) exposed a number of welded plain carbon steels, including A285 (a common digester steel) and several other steels, to  $H_2S$ -containing salt brines in oil refinery applications. The A285 steel was immune to sulfide cracking after an 18-month exposure, as were the other steels whose hardnesses were below  $R_C$  22 (and whose tensile strengths were below 110 ksi). Others have shown that steels that satisfy the NACE criteria can crack, but only in the most aggressive acid sulfide media (13, 14).

Welds may or may not be more susceptible than base metal to sulfide cracking. In most cases, sulfide cracking is observed in the heat-affected zone (HAZ) of welds when the local hardness in this zone exceeds  $R_C$  22. However, the tests described above involving A285 -- a digester vessel material -- did not crack in the as-welded condition, even though the local hardness in the HAZ slightly exceeded the  $R_C$  22 criteria (12).

Cracking occurring in acidified sulfide media is generally branched and transgranular, in contrast to the branched intergranular cracking reported in most examinations of digester cracks. This difference in crack morphology also argues against a sulfide cracking mechanism for digester weldments.

Finally, as described in a later section, there is no strong correlation between cracking susceptibility and acid cleaning practices.

Thus, the circumstantial evidence against cracking via a sulfide/hydrogen - embrittlement mechanism is convincing. The evidence is:

- (i) Questionable acidification of condensate on vessel walls during acid cleaning of the lower vessel
- (ii) Low susceptibility to sulfide cracking exhibited by low-strength steels in the digester steel grades
- (iii) Transgranular cracking morphology for sulfide cracking versus intergranular cracking in digester weldments
- (iv) No correlation between acid cleaning frequency and cracking.

Although some tests might be appropriate to resolve unequivocally the question of susceptibility of digester-type weldments to sulfide cracking, the available evidence suggests that digester cracking is not a consequence of acid sulfide cracking during acid cleaning.

#### The Potential for Carbonate/Bicarbonate Cracking

Parkins and his co-workers have shown that carbonates (specifically aluminum carbonate) and mixtures of sodium carbonates and sodium bicarbonates can cause stress corrosion cracking of a variety of low-strength steels (15, 16, 17, 18). Similar results have been reported by Herbsleb et al. (19) and Wender-Kalsch et al. (20, 21) Cracking in carbonate/bicarbonate solutions is intergranular, as is cracking in continuous digester weldments. SCC is observed in a variety of  $\text{CO}_3^{=}/\text{HCO}_3^{-}$  mixtures with pH values in the range 8 to 10.5. As little as 0.25N  $\text{Na}_2\text{HCO}_3$  (bicarbonate) will cause SCC in steels, but 2N  $\text{Na}_2\text{CO}_3$  (carbonate) will not induce cracking at 22°C or at 90°C. Stress corrosion cracking occurs only within a narrow range of potential (-0.625 to -0.45 VSCE) which is slightly more positive than the potential for cracking in caustic. As

seen in subsequent chapters, this potential range cannot easily be reached by digester steels exposed to kraft liquors. Herbsleb (19) has reported that a pipeline steel was susceptible to SCC under slow extension rate conditions, whereas statically loaded specimens in the same solutions at the same potentials did not show any cracking.

Since carbonate/bicarbonate cracking is a relatively new phenomenon, the available information is inadequate to determine whether this type of cracking has a role in digester cracking. What little information is available suggests that carbonates are not directly involved in digester cracking. Carbonate/bicarbonate cracking has not been reported in the pH range (12-14) associated with kraft cooking liquors; Sutcliffe et al. (15) reported cracking only below a pH of 10.5. Moreover, most kraft liquors contain carbonate only in concentrations at or below the lower threshold for cracking in SERT tests (0.25 N  $\text{Na}_2\text{CO}_3$ ). At the high pH of the kraft cooking liquors, nearly all of the carbonate/bicarbonate ions will exist as alkali carbonate since  $\text{pK}_2$  is  $\sim 10$  for  $\text{H}_2\text{CO}_3$ . Strongly alkaline carbonate solutions do not appear to be potent SCC activators that characterize less alkaline  $\text{CO}_3^{2-}/\text{HCO}_3^-$  mixtures.

In the final analysis, it must be acknowledged that carbonates/bicarbonates are known to induce SCC in low-strength steels, but the role of these species in cracking associated with kraft liquors cannot be judged because of the scarcity of relevant data. An experimental assessment of the role of carbonates in digester cracking would be required to resolve this issue unequivocally.

## SCC of Carbon Steels in Caustic Solutions

### Service Performance

Plain carbon steels are wellknown for their susceptibility to intergranular stress corrosion cracking in caustic. The problem first became apparent in the early part of this century when a number of riveted, high-pressure steam boilers failed (22, 23). In subsequent years, a number of failures have occurred in components and structures as a result of stress corrosion cracking of steel in caustic solutions.

Schmidt et al. (24) have summarized the results of a 1951 survey of caustic cracking experience, in which a variety of tanks, evaporators, pipes, and related equipment failed after exposure to caustic soda. Welds were a common site for caustic cracking. In many cases, cracking was observed after 10 or 15 years of successful operation, whereas in other cases, cracking took place in a few months. A variety of different steels exhibited cracking, including one welded vessel fabricated from A-285C steel -- a common steel used in fabrication of continuous digester vessels. Most failures were reported after exposure to concentrated caustic solutions containing more than 30% caustic.

Based on their field measurements, Schmidt et al. (24) identified regions where the temperature and NaOH concentration would and would not cause cracking of carbon steel. As shown in Fig. 14, only two failures were reported in solutions containing 10% or less sodium hydroxide, both of which occurred above 200°F. The beneficial effects of stress relief of weldments were also cited.

In the years since Schmidt reported the results of his survey, caustic cracking has been reported in a variety of carbon steel structures, a few of which are described below. Ashbaugh (25) described a number of instances of

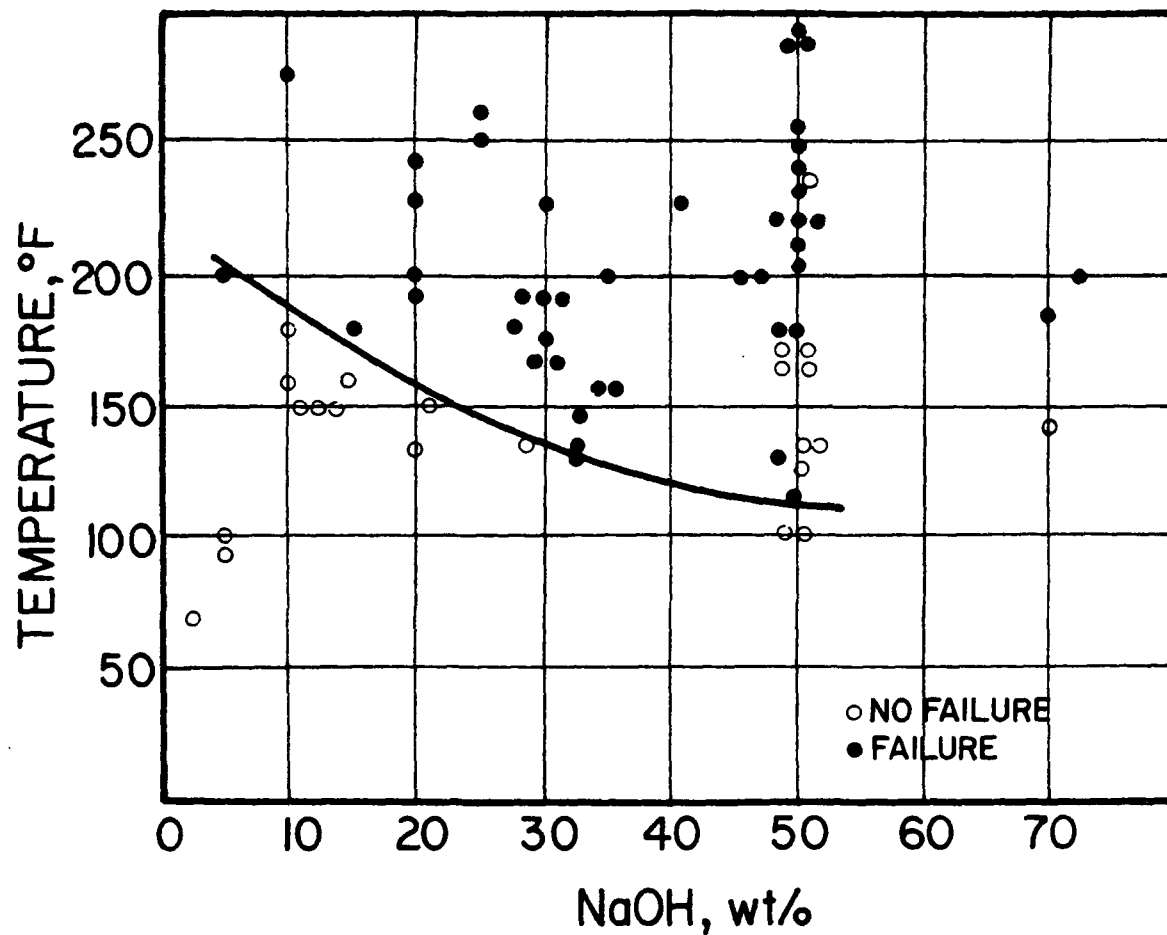


Figure 14. Zones of caustic cracking susceptibility in carbon steels.

caustic cracking in petrochemical plants, most of which were associated with contaminated steam systems and piping for handling caustic. Stress corrosion cracking of disks in steam turbines has been attributed to caustic cracking in the highly stressed areas at the keyways and blade attachment areas (26,27). Longitudinal cracking in a welded joint in a caustic soda evaporator was reported by Naumann and Spies (28). Stress corrosion cracking was also reported in the welds of carbon steel dissolving tanks used in the alkaline Bayer process (29,30). These tanks were filled with a sodium aluminate solution whose NaOH concentration is 100-150 grams/liter -- which is close to the caustic levels in kraft liquors -- in the temperature range 45-60°C.

In view of digester cracking conditions, it is interesting to note that Artem'ev et al. (29) implicated dissolved sulfur compounds as the key factor in rapid weld cracking of Bayer process dissolving vessels. Vessels which crack rapidly were found to contain as much as 3.5 g/L of total sulfur in various states of oxidation, whereas those vessels with long service experience had only 0.08 g/L total sulfur. Laboratory tests indicated that the sulfur compounds prevented the passivation of the steel walls of the dissolving tanks and maintained the potential in the regime for cracking. Treatment of the dissolving liquor with a strong oxidant -- hydrogen peroxide or potassium persulfate -- oxidized the sulfur components to an innocuous state, which allowed passivation and protection of the vessel from cracking.

In 1967, the NACE published its Corrosion Data Survey (31) -- a compendium of corrosion and stress corrosion cracking experience, including SCC in hot caustic solutions. Based on these findings, a recommendation was made regarding materials of construction in contact with hot caustic. As shown in Fig. 15,



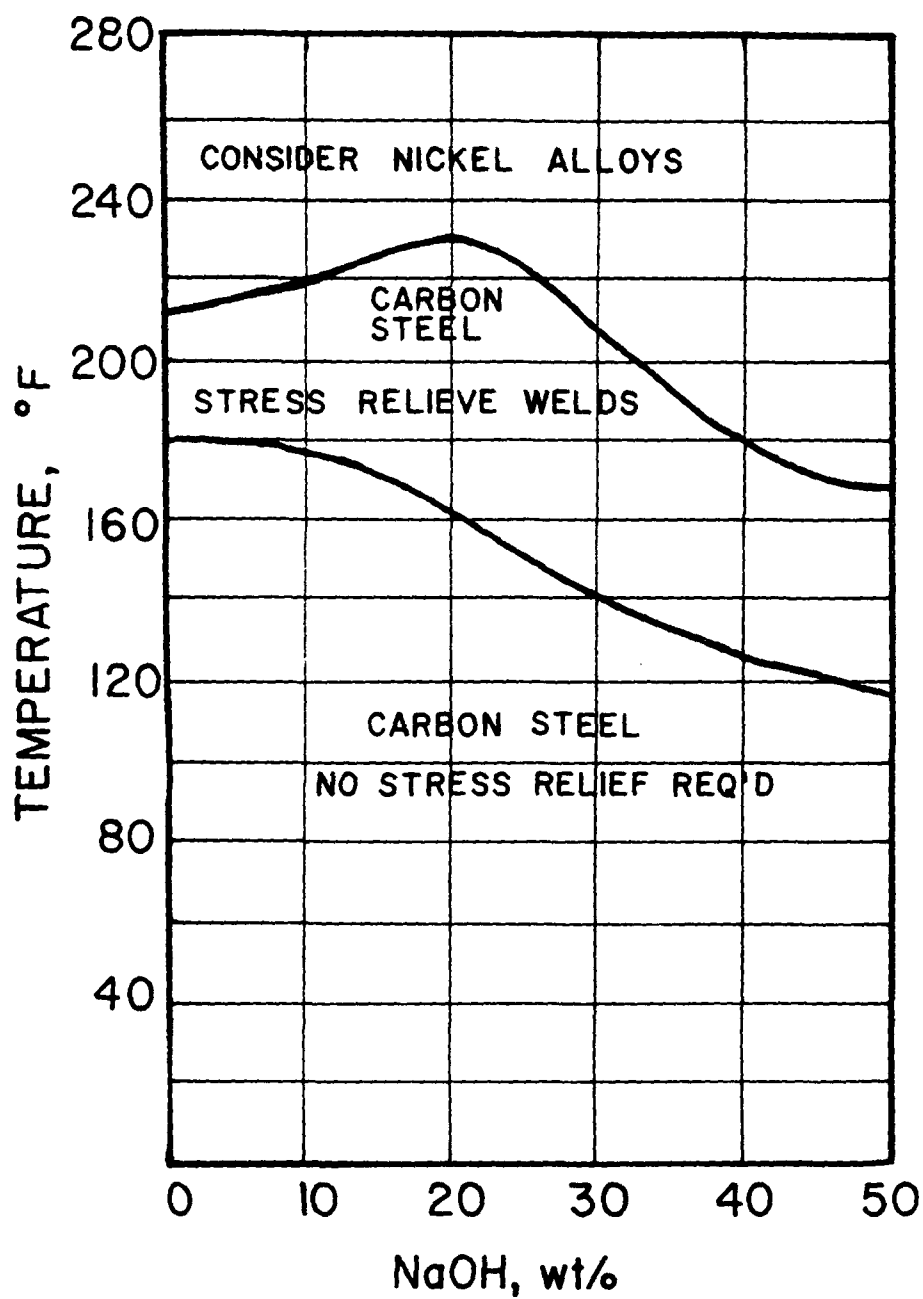


Figure 15. Materials recommendations for service in caustic media (Corrosion Data Survey).

materials recommended included carbon steel without stress relief at low temperatures, carbon steel with stress relief of welds and other highly stressed areas at intermediate temperatures, and the use of nickel alloys at still higher temperatures.

To summarize, stress corrosion cracking of carbon steels in contact with hot caustic solutions continues to be a problem of recurring concern. Welds appear to be particularly susceptible to caustic cracking, but this susceptibility can be decreased by an appropriate stress relief treatment of the welds.

#### Reviews of Caustic Cracking

There have been several review articles published recently which summarize the results of laboratory and field investigations of caustic cracking of plain carbon steels (2,3,4,32,33). A voluminous literature is cited, since there have been numerous investigations on this subject. The salient features of caustic cracking studies relevant to digester cracking are cited in the paragraphs to follow, but a detailed summary of caustic cracking is beyond the scope of this report. The reader is referred to the review articles and the cited literature for more information.

#### Caustic Cracking Morphology

The usual morphology of caustic cracking in carbon steels involves an intergranular crack path, with occasional reports of mixed intergranular/transgranular growth. The crack path in quenched and tempered steels follows prior austenite grain boundaries, whereas in ferritic-pearlite steels, the path generally follows ferrite-ferrite boundaries, with occasional growth along the interface between ferrite and pearlite colonies (34,35).

### NaOH Concentration

Stress corrosion cracking occurs in caustic solutions over a wide range of compositions, ranging from 5% to more than 70% NaOH. Cracking appears to be most severe in the intermediate caustic range, near 30% NaOH. In some tests of short duration, lasting only a month or so, the range of NaOH concentrations causing cracking is compressed to 20-35% NaOH (36). Based on these results, Berk and Waldek (36) identified a "caustic danger zone" where temperature and caustic concentrations were likely to cause stress corrosion cracking.

The cooking liquors used in continuous digesters have a caustic concentration that is at the lower extreme of that causing caustic cracking. Cooking liquors entering the vessel contain about 5% NaOH, plus an additional caustic contribution from hydrolysis of  $\text{Na}_2\text{S}$ , so a hydroxide concentration corresponding to about 8% NaOH is typical. Based on this low caustic concentration alone, exposure of carbon steels in kraft cooking liquors may require long incubation times or imposed potentials to induce caustic cracking.

### Temperature

Caustic cracking of carbon steel occurs over a wide range of temperatures, with the lower temperature threshold for cracking dependent on the caustic concentration (Fig. 14). At low caustic concentrations, a higher temperature is required for cracking, according to the field data reported by Schmidt et al. (24). At higher concentrations of caustic, however, no correlation could be found relating temperature and time-to-cracking. Bohnenkamp (4) and others (37) have confirmed the inverse relationship between temperature and time-to-failure in laboratory tests at controlled potentials.

Since autoclave testing is required for caustic cracking studies at temperatures above the atmospheric boiling temperature, there have been few

laboratory studies of caustic cracking in plain carbon steels at digester operating temperatures. Robinson and Nel (38) examined the effect of temperatures as high as 250°C (482°F) and concluded that cracking susceptibility in 50% NaOH decreased as temperatures increased from 210°C (410°F) to 240°C (464°F). For a mild steel exposed to 33% NaOH, Singbeil and Tromans (39) found that the stage II crack velocity decreased logarithmically as 1/T increased (Arrhenius behavior). That is, crack growth rates increased with increasing temperature, with an apparent activation energy of 24 kJ/mol. Berry (40) also reported Arrhenius behavior for crack velocities obtained with a quenched and tempered steel exposed to 33% NaOH at temperatures ranging from room temperature to as high as 115°C (240°F).

Temperature is also known to affect the rest potential for some steels exposed to caustic solutions; in some instances, temperature determined whether the rest potential resided within the range of potentials required for cracking. For example, McCord et al. (27) found that the rest potentials of two quenched and tempered steels remained in the cracking range during exposure to 28% and 35% NaOH solutions in a temperature range of 60°C (140°F) to 120°C (248°F). In a 20% NaOH solution, however, one of the steels exhibited a rest potential 600 mV above the cracking zone at temperatures from 60°C (140°F) to 85°C (185°F). The potential fell to within the cracking range only above 85°C (185°F).

To summarize, most studies of temperature effects in caustic cracking of carbon steels have been conducted below the range of temperatures that exist in continuous digesters. At these lower temperatures, there is every indication that caustic cracking obeys thermally activated kinetics; i.e., crack velocities increase exponentially with increasing temperature. Above the atmospheric boiling temperature, little is known about the SCC of plain carbon steels in

caustic, although there has been a continuing effort to characterize caustic cracking of stainless alloys and quenched and tempered steels at elevated temperatures.

### Potential

It is now well established that caustic stress corrosion depends strongly on the electrochemical potential of the carbon steel immersed in the caustic solution. Several reports have shown that caustic cracking occurs only within a small range of potentials which are slightly noble to the anodic peak at the active-passive transition (2,4,32,33). The range of potentials is broadened as the concentration of sodium hydroxide is raised, as shown in Fig. 16, with the mid-range potential for cracking located at approximately -0.7 VSHE. Bohnenkamp (4) found that the potential region associated with cracking did not vary as the temperature was increased from 70°C (158°F) to 120°C (248°F); the latter temperature is relevant to cracking in digesters.

Although the potential region associated with cracking of carbon steels appears to be relatively independent of the composition of the steel, Parkins (2) does report that carbon steels containing Si and Mo can exhibit unusually wide potential regions where cracking is observed. In some cases, a second zone of cracking is reported at a higher range of potentials, as shown for the case of a quenched and tempered Cr-Mo steel in Fig. 17 (41). Parkins (2) also reports that the potential required for caustic cracking depends on the carbon content of the steel.

The rest potentials for carbon steel may or may not reside within the range required for cracking, which may explain why some investigators report difficulty in cracking steels in the laboratory without imposed potential.

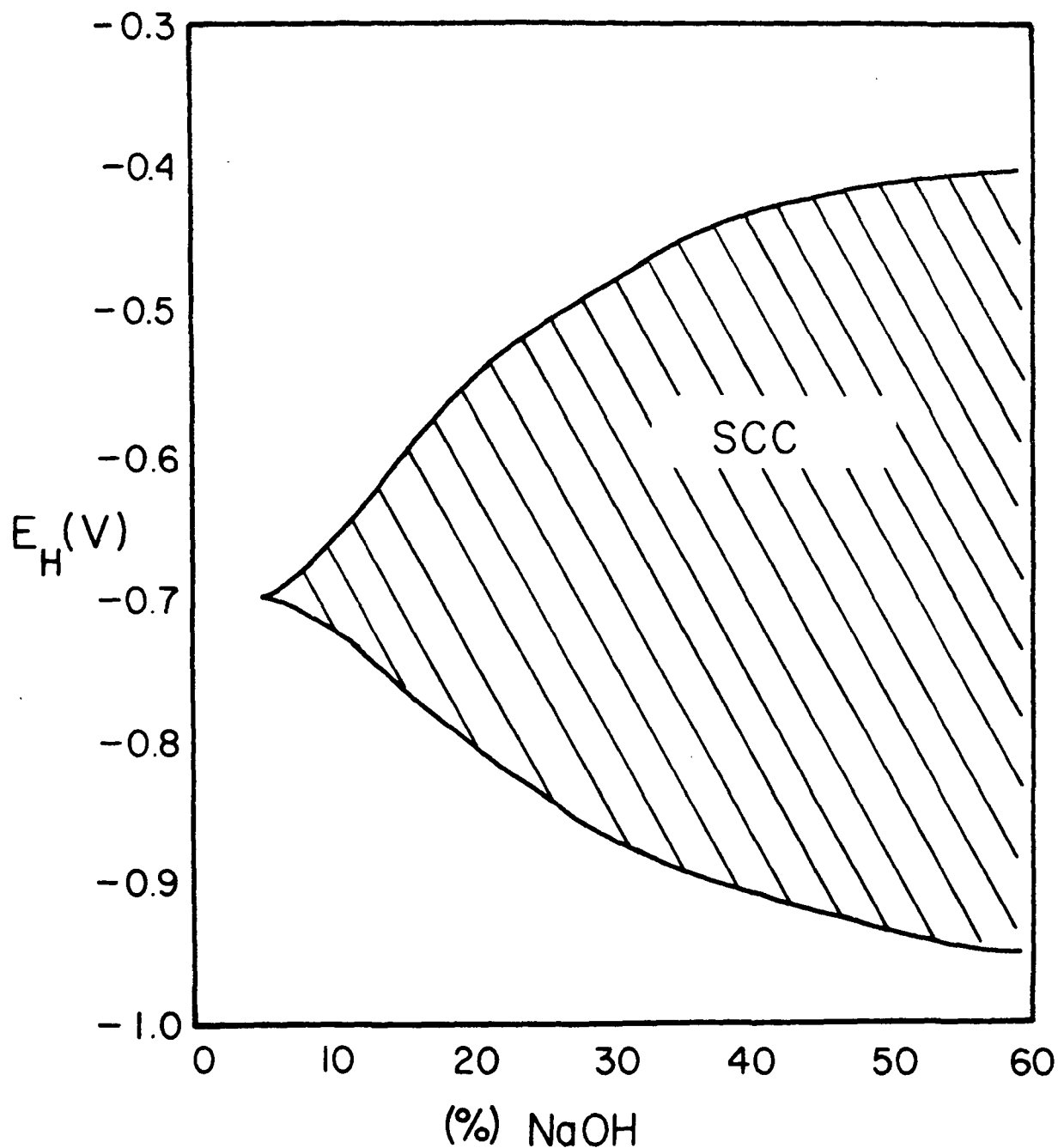


Figure 16. The range of electrochemical potentials for caustic cracking of carbon steels [Parkins (2)].

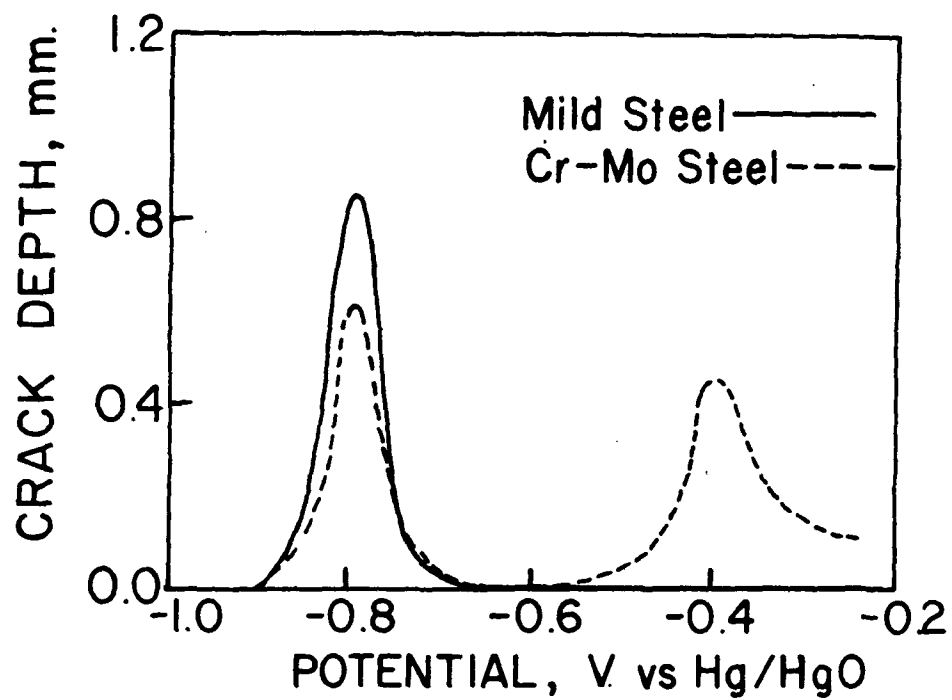


Figure 17. The electrochemical potential dependence for caustic cracking susceptibility of two steels.

Reinoehl and Berry (32) found the initial potential of a steel immersed in caustic at 93°C (200°F) was well above the range of potentials required for cracking, but drifted downward as time elapsed. The rate of downward drift of potentials varied with time, depending on the caustic concentration; above 20% NaOH, the potentials drifted downward into the cracking regime, and SCC was observed. Below 20% NaOH, the rest potential occurred well above the regime associated with cracking, and no SCC was observed. Humphries and Parkins (42) and Harrison, et al. (41), on the other hand, reported that their specimens were initially active when immersed in caustic, with a potential of  $\sim 0.900$  VSHE, but the potential drifted upward, through the cracking range in some cases. An example of the change in potential with time is shown in Fig. 18. The drift behavior of the open circuit potential apparently depends on many factors, including composition of the steel, surface preparation, and caustic concentration. (The role of oxidizing species is addressed below). When investigations fail to produce caustic cracking in laboratory circumstances without impressed potentials, it is likely that the potential of the steel does not spontaneously reside within the critical cracking regime for a sufficient period of time to permit crack initiation and growth.

Several investigators have pointed out that the critical regime for cracking in caustic coincides with the zone where magnetite ( $\text{Fe}_3\text{O}_4$ ) is the stable solid in equilibrium with sodium hydroxide, and the  $\text{HFeO}_2^-$  ion is the stable dissolved species. The Pourbaix (43) diagram for iron shown in Fig. 19 indicates that the regions of stability of these species coincide with the caustic cracking regime. Bohnenkamp (4) cites evidence that the surface film stable at  $-700$  mVSHE is magnetite, whereas  $\gamma\text{-Fe}_2\text{O}_3$  forms at higher potentials, approximately  $-300$  mVSHE. The magnetite ( $\text{Fe}_3\text{O}_4$ ) film is implicated in cracking,



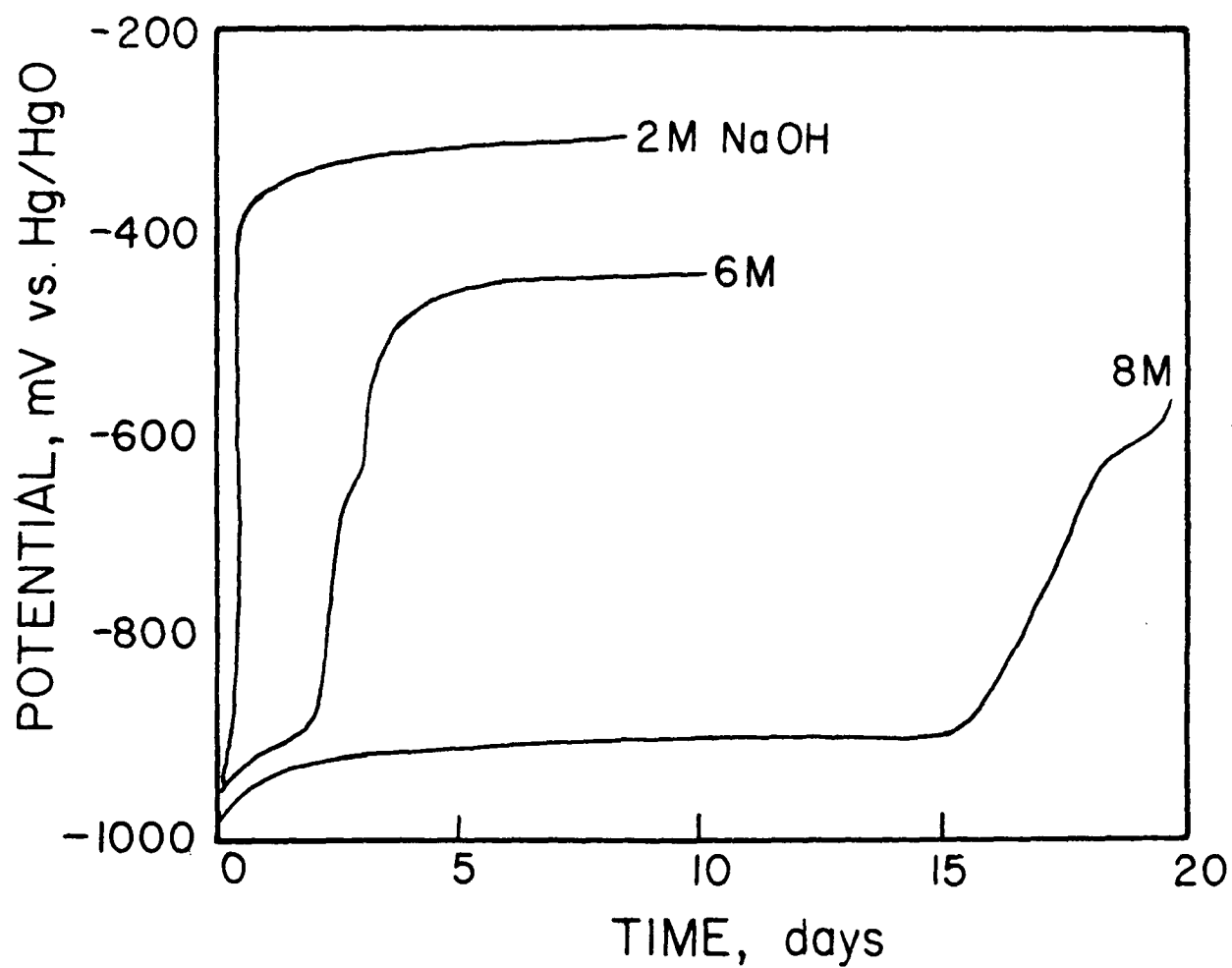


Figure 18. Upward drift in rest potentials for a Cr-Mo steel immersed in two caustic solutions.

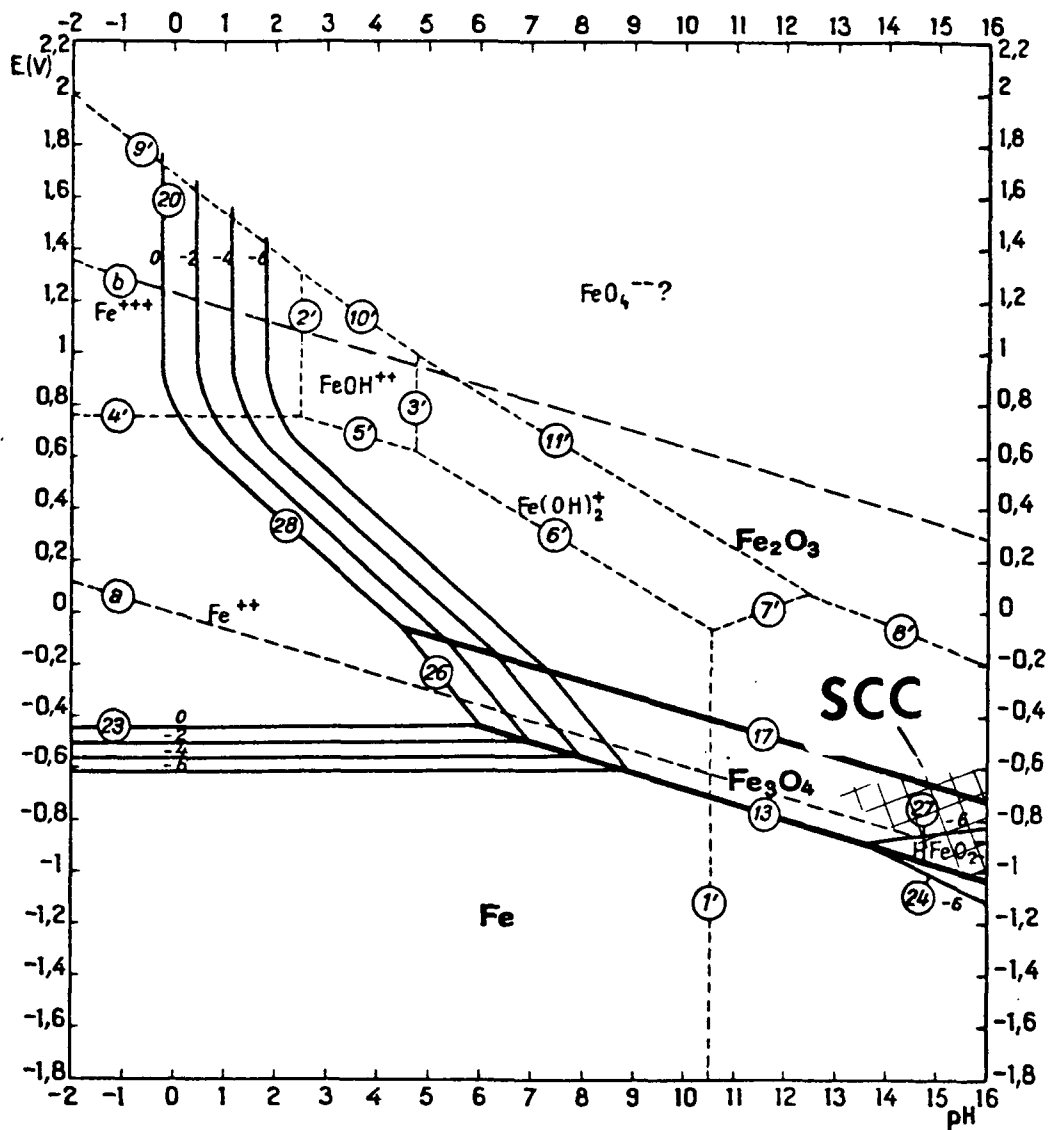


Figure 19. Pourbaix diagram for iron showing the range where caustic cracking is observed [Pourbaix (43)].

in contrast to the hematite ( $\text{Fe}_2\text{O}_3$ ) film formed at higher potentials, because the magnetite film is thought to be much less ductile than hematite (44) and therefore more likely to rupture during crack tip deformation. The dihypoferrite ion ( $\text{HFeO}_2^-$ ), is the soluble product of the active dissolution that follows the rupture of the film at the crack tip. When the solubility product of the  $\text{HFeO}_2^-$  is exceeded,  $\text{Fe}_3\text{O}_4$  is precipitated, and the crack tip is repassivated by the magnetite film to await another film rupture event.

#### Stress/Stress Intensity

Stresses high enough to induce plastic deformation at some point in the surface of the test specimen are required for the onset of stress corrosion cracking in unnotched carbon steel specimens, according to Robinson and Nel (38) and Bohnenkamp (4). Stress intensities as low as  $18 \text{ MPa } \sqrt{\text{m}}$  ( $16.4 \text{ ksi } \sqrt{\text{in}}$ ) can induce crack growth at  $10^{-10} \text{ m/s}$  (0.1 inches/year) in mild steel, according to Singbeil and Tromans (39). Similar, but somewhat lower, threshold stress intensities are reported for quenched and tempered steels (2). Apparently, some localized plastic deformation is required to induce film rupture and subsequent crack growth.

#### Metallurgy

Parkins (2) concludes that all plain carbon steels are susceptible to caustic cracking, but some steels are more prone toward caustic cracking than others.

The effect of carbon content on caustic cracking of iron and steel is somewhat controversial. Robinson and Nel (35) concluded that a high carbon content was detrimental since high carbon, fully killed steels were most susceptible to cracking, whereas intermediate carbon, semikilled steels and lower

carbon rimmed steels were much less prone to caustic cracking. A zone-refined iron specimen, presumably with a very low carbon content, would not crack under the most aggressive caustic conditions. On the other hand, Bohnenkamp (4) could not induce caustic cracking in a high carbon (0.33 C) steel under conditions which would readily crack low carbon Armco iron. Mazille and Uhlig (37) found that increasing the carbon content from 0.09% to 0.24% decreased the time to failure at 85°C (185°F), 105°C (221°F), and 125°C (257°F). The opposite behavior was reported by Hugo et al. (45), who found that 0.02% C steel cracked readily in boiling 35% NaOH, whereas higher carbon steels (0.17% C, 0.39% C) also stressed above yield were virtually uncracked. Zhagalaya et al. (46) found that high carbon steels (0.35 - 0.45 C) were more resistant to caustic cracking than low carbon steels (0.04 to 0.20 C), but all of the steels did exhibit caustic cracking. Additions of titanium to low carbon steels to reduce the dissolved carbon content by TiC precipitation increased the resistance to caustic cracking (4,47). In one study (47), the reduction in dissolved carbon did not stop the initiation of cracks, but rather impeded the growth of cracks. Parkins (2) has suggested that caustic cracking of plain carbon steels might be avoided by using carbon contents exceeding 0.2%.

Relatively little is known about the role of metallurgical structure on caustic cracking susceptibility, which is surprising in view of the susceptibility of welds to caustic cracking in service. Both quenched and tempered steels and ferritic-pearlitic steels exhibit cracking in similar ranges of potential, according to Harrison et al. (41). Parr and Straub (23), in some of the early work on caustic cracking, reported cracking of a variety of early steels in caustic. In this study, "Flange steel" -- a predecessor of modern day A-285 steels -- exhibited cracking regardless of whether or not the structure was ferritic-pearlitic, martensitic, or spheroidic. Johnston and McCord (48) also

examined alkaline sulfide cracking of pearlite, bainitic, and martensitic structures in a Cr-Mo-V steel. As-quenched martensite was susceptible to cracking at potentials cathodic to hydrogen, but none of the other structures exhibited a significant degree of cracking in the alkaline sulfide media (0.6 M Na<sub>2</sub>S). The as-quenched martensite was also found to be immune to caustic cracking in 0.6 M NaOH solution. Hurst and Cowen (49) reported that tempering a martensitic 2-1/4 Cr-1 Mo steel reduced the range of potentials where caustic cracking could be induced at 116°C (240°F). These authors also examined caustic cracking in weldments exposed to 30% NaOH over the temperature range of 50°C (122°F) to 300°C (572°F) and found that as-welded structures exhibited a high degree of susceptibility to caustic cracking, as did as-quenched structures. Cracks were usually confined to the base metal adjacent to the weld, and to the fusion line.

#### Effects of Additional Species

Species added to caustic solutions appear to affect caustic cracking in one of two ways: (i) the chemical species play a direct role in film stability or dissolution characteristics, or (ii) the chemical species affects the rest potential relative to the potential range for cracking. These two effects can be discriminated by conducting tests at controlled potentials, as done by Humphries and Parkins (42). These investigators found that PbO, Pb<sub>3</sub>O<sub>4</sub>, and ZnO additions had little effect on when tests were performed at controlled potentials, rather than the rest potential.

Aeration of the caustic solution had a beneficial effect on cracking susceptibility independent of potential, as did additions of Na<sub>2</sub>SiO<sub>3</sub>. On the other hand, Na<sub>2</sub>HPO<sub>4</sub> additions completely suppressed caustic cracking over the complete range of potentials normally causing cracking in 35% NaOH solutions, as did additions of two organic inhibitors, valonea and quebracho.

Several authors have shown that caustic cracking can be promoted or retarded by the addition of salts and other species that affect the rest potential achieved in caustic solution. Lead monoxide added to caustic is particularly effective in promoting caustic cracking (30,37,50), largely because the rest potential in the presence of PbO resides within the potential range for cracking (42). Oxidizing species such as permanganates also affect the rest potential in caustic but do not promote cracking because the rest potential resides above the critical range for cracking. In the case of a NiCrMoV steel exposed to 40% NaOH, Shalvoy et al. (51) reported that the caustic cracking susceptibility was slight unless salts were added that raised the rest potential into the cracking range above 800 mV.

#### Cracking Kinetics

When smooth specimens are exposed to caustic under high stress and at the correct potential for cracking, the rate of cracking can be very rapid indeed. Failure times as short as a few hours have been reported for laboratory coupons. At the periphery of the potential range for cracking, failure times of hundreds of hours are more typical. Beyond the cracking range, of course, no cracking occurs at all.

Stage II crack growth rates in the range  $10^{-9}$  to  $10^{-8}$  m/s (1.1 to 11 inches/year) have been observed for mild steel specimens exposed to 33% NaOH at the rest potential (39). The higher growth rates were observed at 115°C (240°F) and the lower velocities at 50°C (122°F). Stress intensities above 20 MPa  $\sqrt{m}$  (18.2 ksi  $\sqrt{in}$ ) were required to achieve Stage II velocities. Crack growth rates increased by an order of magnitude when the specimens were held at a potential of -0.76 VSHE -- in the middle of the potential range for caustic cracking.

### Controlling Caustic Cracking

Based on the preceding information, it is clear that caustic cracking can be controlled in carbon steels by (i) reducing tensile stresses, (ii) shifting the metal potential out of the cracking regime, (iii) adding appropriate inhibitors such as quebracho, or (iv) reducing caustic concentration. The most common method for effectively reducing tensile stresses associated with fabrication (welding stress, fit-up, etc.) has been stress relief or replacement components (24). Shot peening of welds has effectively stopped caustic cracking in some cases (49,52), but not in others (30). Shot peening, of course, introduces a compressive layer in the surface of the peened metal, thereby preventing initiation under residual stresses left by fabrication. In one case (30), cathodic protection was used to adjust the potential of a tank that had cracked in a caustic solution and had been repaired by welding. Subsequent failure of the tank occurred because of cracking by the caustic residue on the outside of the tank.

### SCC in Alkaline Sulfide Media

Recent studies by Singbeil and Tromans deserve special consideration because of their emphasis on caustic cracking in an alkaline sulfide medium representative of kraft white liquor (39,53,54,55). These studies have shown that stress corrosion cracking in alkaline sulfide media resembles caustic cracking in most respects, with only small differences in the potential cracking range and anodic current densities.

In agreement with earlier results of Wensley and Charleton (56), Singbeil and Tromans (53) found that the substitution of approximately one-half mole of NaOH with Na<sub>2</sub>S in a 3.5 M caustic solution had only small effects on the electrochemical behavior of an AISI 1018 carbon steel. The addition of the

sulfide caused an increase in the current density at the anodic peak, associated with the active-passive transition, as well as a small shift (to more noble potentials) of the peak passivating potential. An increased temperature [in the range 50°C to 115°C (128 to 240°F)] also shifted the peak passivating current density toward higher currents. The sulfide additions also caused an increase in the current density in the passive range for potentials more noble than -0.4 VSHE. Apparently, no measurements of changes in the rest potential with time were made. In all, the changes in electrochemical behavior caused by the sulfide additions were relatively subtle.

Tromans (55) concluded that the electrochemical processes associated with the active and passive processes were fundamentally the same, with and without sulfide additions. The anodic peak was attributed to the formation of the dihypoferrite ion ( $\text{HFeO}_2^-$ ) during active dissolution of the iron in caustic and caustic sulfide media. The passivation at approximately -0.7 VSHE was attributed to the formation of a magnetite film, although this film was obscured in the case of caustic sulfide tests by the presence of a porous iron sulfide deposit on the metal surface. The increased current density with caustic sulfide in the passive range above -0.4 VSHE was attributed to the oxidation of sulfur species via an unknown reaction.

Slow strain rate tests in caustic and caustic sulfide under controlled potential conditions revealed a narrow zone of potential where caustic cracking was evident. With and without sulfide, the potential range for caustic cracking was only a hundred millivolts wide, as is typical for SCC in relatively dilute caustic solutions (2). As shown in Figs. 19-20, the SERT tests revealed caustic cracking in the range -0.70 to -0.820 VSHE in caustic, and in the range -0.60 to



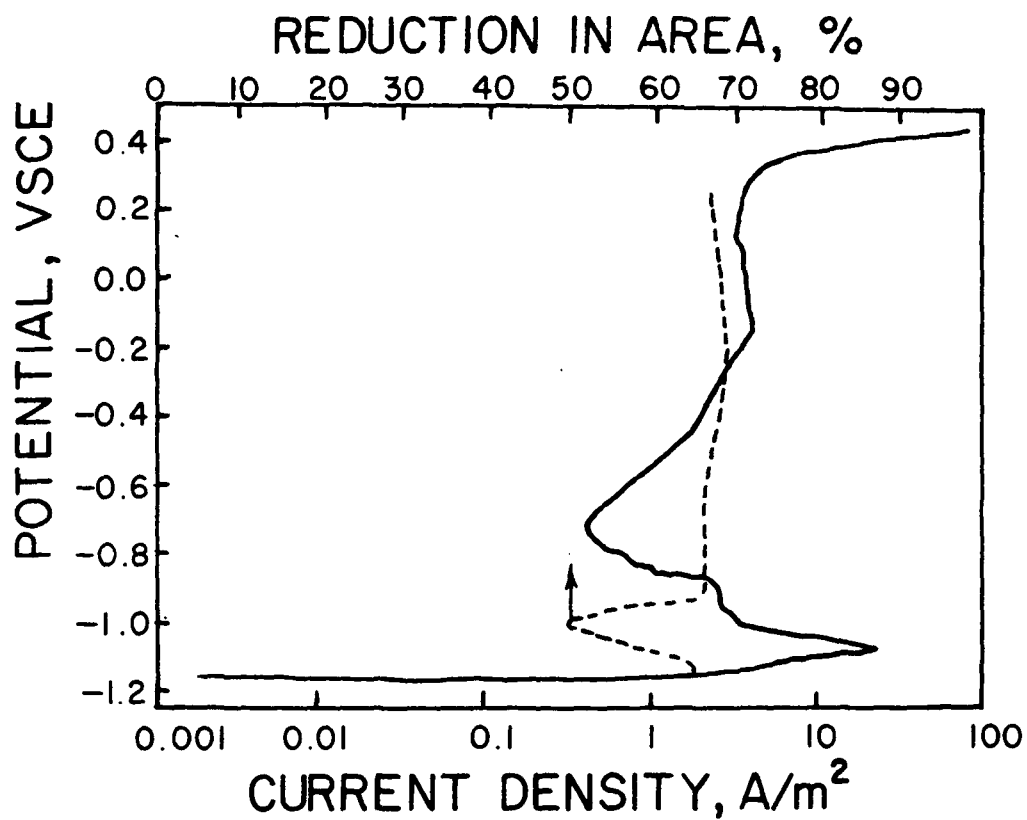


Figure 19. SERT test results showing the potential range for SCC in a caustic solution simulating white liquor [Singbeil & Tromans (53)].

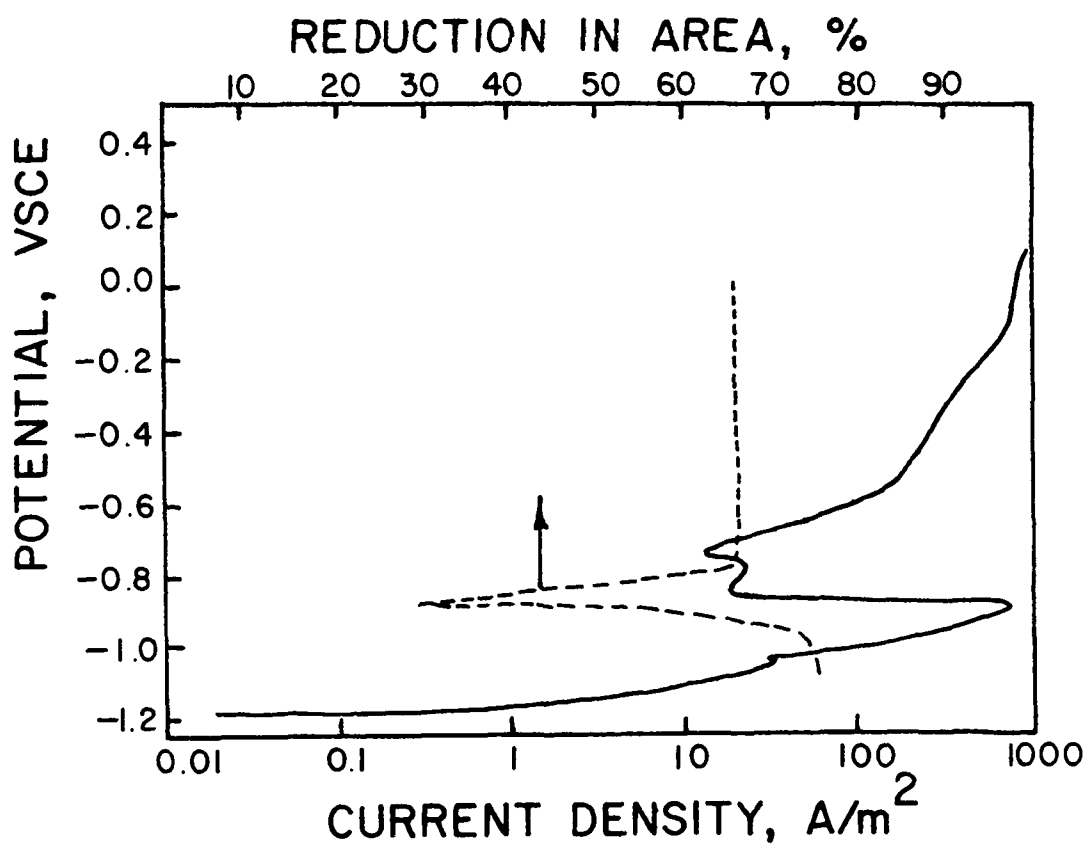


Figure 20. Coincidence of the active-passive transition and the potential range for SCC of carbon steel in a caustic sulfide media.

-0.70 VSHE in caustic sulfide tests. Extensive secondary cracking and intergranular fracture were associated with the losses in reduction in area. The potentials associated with caustic cracking coincide with the active-to-passive transition observed in the polarization curves.

Complementary studies were conducted to determine the crack growth characteristics in caustic and caustic sulfide media. Precracked, self-loaded crack specimens (DCB type) were exposed to caustic and caustic sulfide solutions at 92°C (and at the peak cracking potential) for 400 hours, followed by crack length measurement and calculation of crack growth rates. The velocity of cracking was calculated by dividing the apparent growth increment by the total exposure time, thereby ignoring any incubation periods preceding resumption of crack propagation. Classical three-stage growth behavior was observed in caustic. The Stage II growth rates ranged from  $2.9 \times 10^{-9}$  m/s (3.3 inches/year) in the caustic to  $8.8 \times 10^{-10}$  m/s (0.9 inches/year) in the caustic sulfide media. Crack growth morphology was intergranular and microbranched, with occasional transgranular growth but no significant macrobranching of the crack.

Crack growth kinetics were consistent with a slip-dissolution mechanism for growth, based on reasonable assumptions about processes occurring at the crack tip. Thermodynamic considerations precluded the operation of a hydrogen-assisted mode of crack growth, since the potential and pH apparently prevented the evolution of hydrogen within the crack tip. However, the potential drop down the crack tip under impressed potentials, as described by Doig and Flewitt (57), was not specifically considered and may alter the conclusion rejecting hydrogen-assisted growth mechanisms.

Thus, with the exception of a small shift in the kinetics of dissolution processes, the best available simulation of stress corrosion cracking in a

digester environment shows a strong resemblance to classical caustic cracking. If this resemblance does indeed indicate that digester cracking is due to caustic cracking, the extensive data base described above for caustic cracking becomes meaningful for consideration of cracking in continuous digester weldments. The electrochemical data generated in actual mill liquors in this program -- to be described in subsequent sections -- will tend to reinforce this view of digester cracking as an instance of caustic cracking modified, to some extent, by the presence of species not specifically considered by Singbeil and Tromans (53).

## STATISTICS OF CRACKING IN CONTINUOUS DIGESTERS

### Introduction

Approximately 140 Kamyr continuous digesters have been placed in operation in North America since the late 1950's. These digesters are all quite similar in design, function, operation, and fabrication history, although some differences exist because of developments in materials and evolution in design. The vessels range from small, 150 ton per day sawdust digesters to large, 1300 ton per day chip digesters. Most Kamyr digesters employ the kraft or soda pulping process, although some vessels are used for sulfite and neutral sulfite semi-chemical pulping as well. The vessels were designed by a single firm, and most were fabricated in the field by a single firm or its Canadian counterpart. Only a few different welding processes were employed in the fabrication of digester vessels. About half of the vessels were completely stress relieved in the field; the balance were not stress relieved or only partially stress relieved.

In spite of the broad similarity of the Kamyr continuous digesters, some digesters have experienced severe, repeated cracking in the weldments of the impregnation zone, while other, similar digesters have escaped cracking altogether. For example, the Pine Hill vessel suffered severe cracking leading to vessel failure while another vessel of the same size, using the same pulping process, fabricated at nearly the same time, has escaped stress corrosion cracking. Thirty-three vessels which were not stress relieved had serious cracking in the impregnation zone of the vessel, whereas eighteen exhibited no cracking at all. Of the stress relieved vessels, seven had severe cracking; 23 had no cracking at all.

The different SCC susceptibilities of nominally similar vessels raises some intriguing questions about possible correlations between cracking and some hidden features of digester operation or fabrication. Is cracking confined to welds made with a certain welding procedure? Is there a correlation between cooking liquor composition and cracking susceptibility? Are vessels which have been immune to cracking likely to start cracking if they inadvertently change operating practices that bring them into a cracking regime? Are there changes in pulping practices which susceptible mills can use to retard future crack growth?

One objective of the IPC program was to search for correlations between cracking susceptibility and details of vessel fabrication, design, or operation. The effort was approached in three ways. First, the TAPPI Task Group survey was updated, computer coded, and then scrutinized for correlations between cracking and general operating practices. Second, six mills -- three susceptible to cracking and three immune -- were asked to cooperate by filling out a detailed questionnaire about pulp mill operation, liquor characteristics, recovery practices, etc., to ascertain whether immune and susceptible mills differed in their pulping practices. Third, these same six mills were visited for on-site chemical and electrochemical characterization of cooking liquors. The third approach is described in a later Section; the results of the first two surveys, together with comments of welding consultants, vendors, inspectors, and insurers, are presented in this section.

Although most readers will be familiar with the Kamyr continuous digester, a brief introduction to the operation and nomenclature of the digester system is presented first for those unfamiliar with the topic. Subsequent

sections deal with a general description of cracking, cracking susceptibility versus vessel fabrication variables, cracking susceptibility versus operation variables, and a summary.

### Kamyr Continuous Digester Systems

Most Kamyr continuous digesters share certain characteristics, regardless of whether they are single vessel hydraulic systems of earlier design or large two-vessel systems of more recent design. In every case, the continuous digester is designed to accept wood chips (or sawdust) on a continuous basis, expose the chips to cooking liquors at temperatures and pressures appropriate for delignification, extract the spent liquors from the cooked chips, and eject the cooked pulp for further processing. In some cases, pulp washing is also accomplished within the continuous digester. Usually, the pulping process is accomplished within a single large pressure vessel, although two vessel systems are also in use. The process is continuous in that the mass of chips moves continuously through the system, with each process occurring on the chips as they pass different stages within the vessel.

A typical single-vessel, hydraulic Kamyr continuous digester is shown schematically in Fig. 21. The key elements of the system include (58,59):

- (i) A system for steaming chips at low pressure
- (ii) A high-pressure feed system that injects chips into the high-pressure process, using cooking liquor as a vehicle
- (iii) A top separator which screens chips from the excess recirculating liquor, and directs them to the impregnation zone of the digester vessel
- (iv) A recirculation system for heating cooking liquor extracted from the chips at screens, and returning the hot liquor to the chip mass for cooking



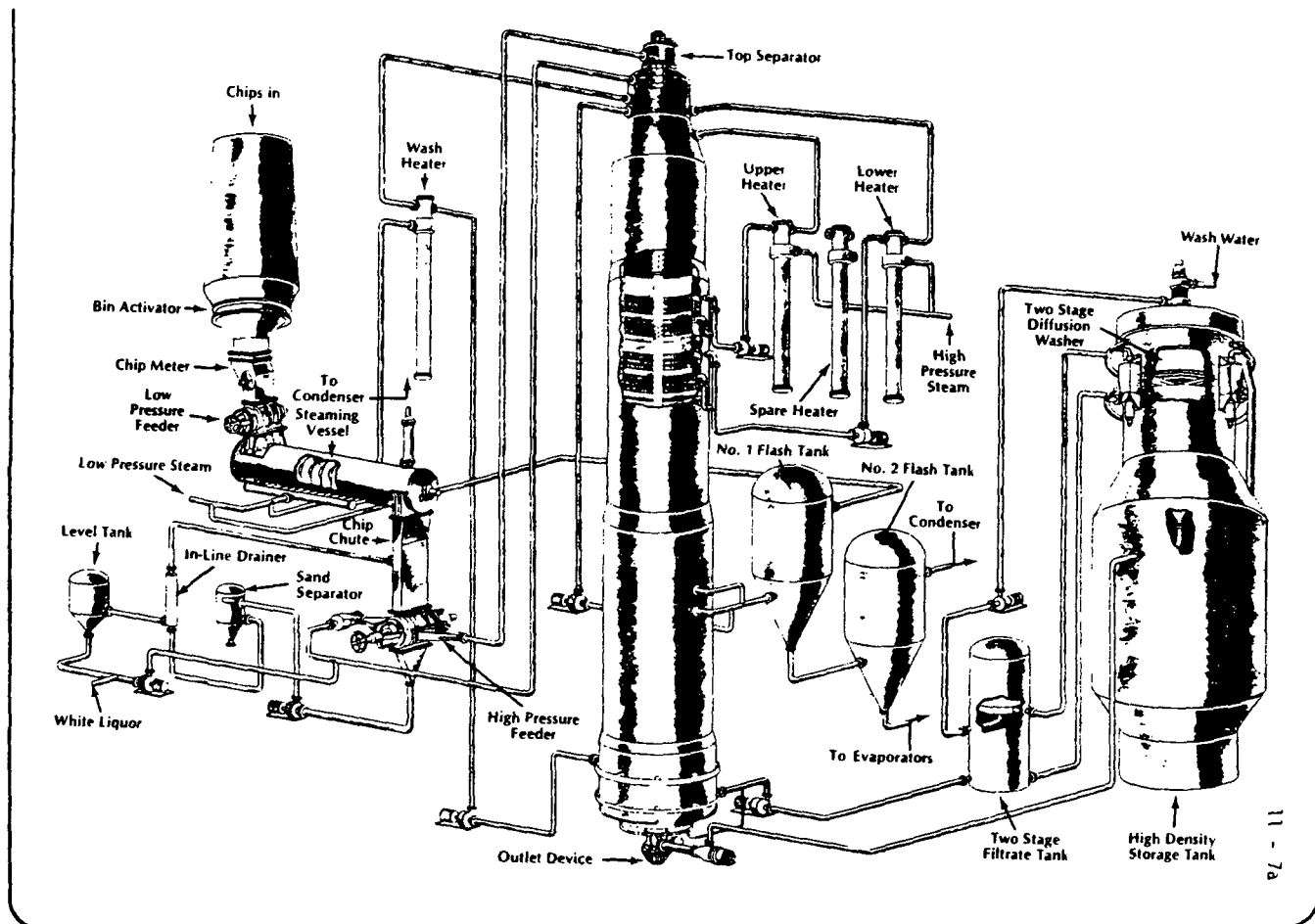


Figure 21. A schematic representation of the basic Kamyr continuous digester design.

- (v) An extraction system for extracting spent liquor from the cooked chips
- (vi) A cooling system for reducing the temperature of the chip mass and for achieving blow consistencies
- (vii) An outlet device which expels the chips to atmospheric pressure

In some cases, washing of the pulp is accomplished in the lower regions of the vessel by injecting and extracting wash waters. In a two-vessel system, the chips are impregnated with liquor first in a small impregnation vessel, followed by cooking in the digester proper. In some cases, the top separator is inverted so that live steam can be directed onto the top of the chip mass in a vapor space at the top of the digester.

Although continuous pulping can be achieved with a variety of processes, only the kraft process is considered here since it is the only process associated with digester cracking. In this kraft process, the chips are first exposed to cooking liquor and condensate in the chip chute following the low-pressure steaming vessel. A recirculating liquor flow is used to pack chips into the pockets of the high-pressure feed mechanism. Liquor is present in the chip chute because of leakage from the top recirculation line at the high-pressure feed pump and from condensate from the steaming vessel. The level in the chip chute is maintained by pumping the excess liquor to the makeup liquor line, where it is mixed with fresh white liquor and pumped into the top circulation flow. As the pocket in the high-pressure feed mechanism is rotated 90° from the chip chute, the chips in the pocket are flushed to the top separator using liquor as a vehicle flowing in top circulation line. At the top separator, the excess liquor from the recirculation flow is screened from the chips and is

returned to recirculation flow. Makeup liquor consisting of fresh white liquor and some excess from the chip chute is added to the top recirculation flow at the top separator or the adjacent piping. The chips are added to the chip mass in the impregnation zone by a rotating screw drive mechanism.

The chip mass slowly passes from the top to the bottom of the vessel, and pulp is removed by the outlet device on the bottom. The uppermost region of the vessel is the impregnation zone, where the chips absorb the cooking liquors entering with the chip mass. As the chip plug moves downward, it enters the cooking zone where temperatures are raised by recirculating heated liquors through the chips in two cook zones. The liquor is extracted at screens on the periphery of the chip mass, whereupon it is heated in heat exchangers and returned to the cook zone via a central pipe perforated at the appropriate cooking zone. Delignification occurs as the chip mass passes through the cooking zones.

Continued descent of the chip plug exposes it to the extraction zone where the spent liquor is removed at screens. Several successive processes involve washing, cooling, and wetting the chip mass preparatory to the blow. The outlet device ejects the cooled pulp in a reversal of the high-pressure feed process. Removal of pulp from the bottom of the vessel allows the chip mass to descend gradually.

Several transitions occur in the digester vessel diameter traversing from top to bottom, as shown schematically in Fig. 22. There is an internal cone at the top of the vessel, with the apex of the cone at the outlet of the top separator. This cone extends to the full diameter of the upper portion of the vessel. Each screen is preceded by a transition in the vessel diameter to provide a plenum for extracted liquor behind the screen, while maintaining constant

chip plug cross-section. Screens, dummy plates, and backing bars are welded to the vessel below each of these transitions. The nomenclature associated with the welds at transitions in vessel diameter is shown in Fig. 22.

Changes in liquor conditions in the impregnation zone where cracking is most prevalent have not been determined. The chips and liquor typically enter this zone at a temperature of approximately 230°F (110°C). The temperature gradually increases as the chips approach the cooking zone. At the top of the cooking zone, the temperature of the vessel will have risen to approximately 310°F (154°C). In the actual cooking zones, the recirculating liquors achieve temperatures of 330°F (165°C), and the full delignification process occurs.

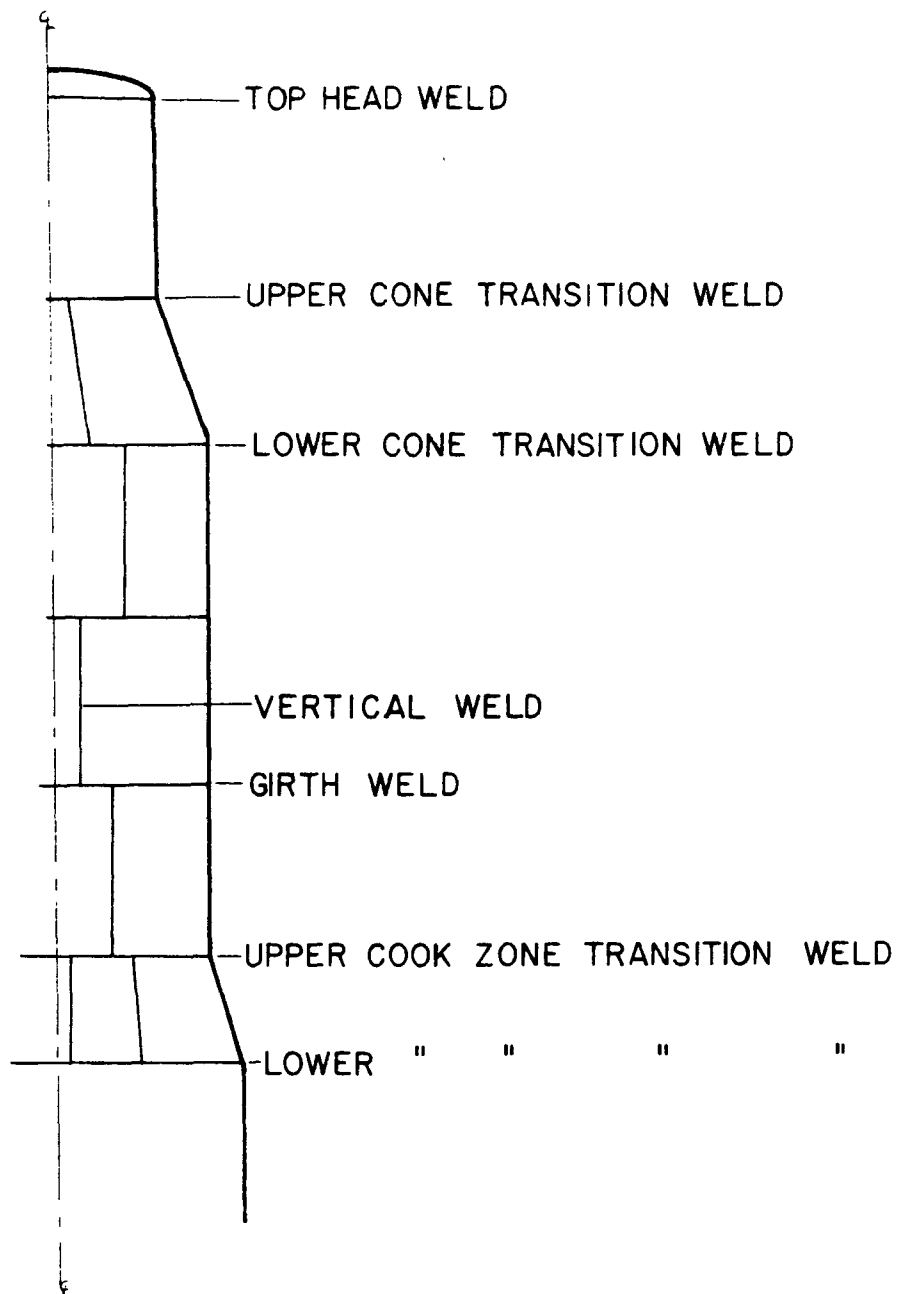


Figure 22. Nomenclature associated with transitions in digester vessel diameter.

### Digester Fabrication

A variety of construction methods have been used in the fabrication of continuous digester vessels. In most cases, the top and bottom heads and the cone section were assembled in the shop using the most convenient and economical welding procedure -- usually shielded metal arc welding (SMAW) with E7018 electrodes because of the complex geometry. Depending on the crane lift capacity and the size of the vessel, some rings were also assembled in the shop by joining half-cylinder sections by SMAW or by submerged arc welding (SAW). For most of the larger vessels, however, vessels were constructed by field welding girth and vertical seams. For smaller vessel sections, the ring was usually fabricated on the ground, lifted into place as a complete ring, and girth welded to the supporting ring. For larger vessels, two or more partial-cylindrical sections were set in place at the horizontal seam, the vertical welds were completed, and then the horizontal girth seam was completed. Transition sections were fabricated from several -- usually six -- prefabricated sections.

During construction of the vessel, the welding engineer and the construction superintendent had some latitude regarding the welding procedure used to complete a given joint, based on economics and practicality. For the largest mechanical erector, the welding engineer at the regional office where the construction was scheduled would control the welding specification for each type of welded joint in the vessel. In the usual case, several welding procedures might be qualified (according to the ASME code and any local codes) for joining specific base metals. For example, for joining A516-70 steel to A516-70 steel, as many as three welding procedures might be qualified for that joint -- one SMAW, one SAW, and a third FCAW-EG (flux cored arc weld - electrogas) procedure. Then, for each A516/A516 welded joint in the vessel, one of the qualified processes would be selected as the preferred method by the regional welding manager.

During construction, however, occasions might arise wherein the intended process might be supplanted by the choice of a different qualified procedure to complete a given joint. As a result, the final record of the actual welding procedure used for any joint will reside in the construction superintendent's reports made during vessel construction.

Virtually all of the welds in continuous digesters (Kamyr type) in North America have been made using one of three welding processes. The following list gives the welding processes and consumables used when most of the digesters were constructed. The consumables do not necessarily represent current practice.

- (i) SMAW This procedure involves "stick" welding with E7018 electrodes (low hydrogen, powdered iron) and a 200°F minimum preheat for sections thicker than 1 1/4". The details of the welding procedure are shown in Table I. This manual procedure has been used, in one circumstance or another, for most types of joints in continuous digester vessels.
- (ii) SAW This submerged arc weld procedure is typically done with Linde 43 wire and Linde Grade 50 flux. The welding procedure is detailed in Table I. This procedure has been used for horizontal welding of girth seams, and for shop welding of various seams in the downflat position.
- (iii) FGAW-EG This electrogas process is a process in which a flux cored wire is fed into a weld pool contained by the plates and a cooled copper shoe, and protected by a CO<sub>2</sub> cover gas. The

TABLE I  
TYPICAL WELDING PROCESSES USED IN DICESTER VESSELS

Procedure	Speed	Electrode	Preheat*	Polarity	Passes	Diameter	A	V	Position	Flux
SMAW	-	E8018 E7010 E6010	200 - 300°F	DCRP	Multiple	5/32" 3/16"	120-310	21-70	All	None
SAW	7-12 ipm	Linde 42	None	DCRP	Multiple**	5/32" 1/8"	480-1050	26-38	Horizontal, Downflat	Linde 50
FCAW-EG	1-4 ipm	Speedalloy 66 Arco Vertomax 70	None	DCRP	2**	7/64"	400-500	32-38	Vertical	CO <sub>2</sub> Shield gas.

\* For welding plates thicker than 1 1/4"

\*\*Manual pass with 7018 first



electrogas process was used exclusively for vertical welds in ring assembly. The copper shoe moved up as the weld is solidified. The flux cored wire used most often was McKay Speed Alloy 66, although other wires have been used. Welding details are outlined in Table I.

The choice of welding procedure for any joint was dictated by convenience, economics, and practicality. SAW welding is preferred for horizontal girth welds because of the high rate of metal deposition. However, the use of SAW requires a simple geometry that allows set-up of the automatic welding machine. Consequently, the girth weld joining a transition ring to the ring immediately below was never made with SAW -- the automatic apparatus could not be set up on the angled surface above the joint. These joints would be field welded by SMAW. The electrogas process was apparently used only for making vertical welds, since the weld pool had to be confined in the groove by the copper shoe and gravity. Electrogas welding of vertical welds in rings was a very common practice after 1965, but was not used before that date. SMAW welding was ubiquitous -- being used when geometry or other concerns prevented the use of a higher deposition-rate process, or when the vessel diameter was small.

Vessels have all been fabricated from low-to-medium strength carbon steels of ASTM type A516-70, A212-B-FBX and A285-C. The compositions and strength properties of these alloys are shown in Table II. In recent years, A516-70 has supplanted A212-B-FBX. In many cases, vessels are constructed from two different steels, with one steel being used for the lower portion and a second steel used for the upper portion of the vessel. All of these steels are carbon-manganese steels with a ferritic-pearlitic microstructure, purchased in the hot-rolled or normalized condition, depending on thickness. Cylindrical

TABLE II  
COMPOSITIONS AND PROPERTIES OF PRESSURE VESSEL STEELS

	A516-70	A-212B-FBX	A285-C
Composition	Percent by weight		
C	0.28 max	0.33 max	0.30 max
Si	0.15 - 0.33	0.15 - 0.33	*
Mn	0.85 - 1.20	0.90 max	0.80 max
S	0.04 max	0.04 max	0.04 max
P	0.035 max	0.035 max	0.035 max
Cu	--	--	0.20 - 0.035
Properties			
Tensile strength	70 - 85 ksi	70 - 85 ksi	55 - 65 ksi
Yield strength	38.0 ksi	38 ksi	30 ksi
Elongation - 2" gage	21%	22%	29%

\*A285-C-MOD is a low Si version of A-285-C, typically with 0.1% Si.

sections are cold-rolled to shape on a three-roll press, without subsequent stress relief or normalizing anneals unless specified by the customer or required by the Code.

Many vessels have stainless clad surfaces included in the construction, at least at the top and bottom head regions. The top and bottom heads are usually clad with 304L stainless steel, according to ASTM SA264-TP304L. Some vessels are completely clad internally with an austenitic stainless steel. Other vessels have clad regions in the area of maximum cooking temperature or in the extraction region.

About one third of the vessels were fabricated with a low silicon version of A285-C in the impregnation zone of the digester vessel. This material, designated A285-C-MOD, has a maximum Si content of 0.10 w/o, whereas no condition for Si content is imposed by the ASTM specification for A285-C. In some of the vessels, the welds were made with a lower Si alloy (E6010 or E7010) in the last passes on the internal welds, so that the weld cap exposed to liquor was low in Si.

Stress relieving of vessels is done according to the minimum requirements of the ASME or local code in force at the time of construction, unless the customer specifies a more extensive stress relief. Generally speaking, the ASME Code now requires that those portions of the vessel thicker than 1.5 inches receive a stress relief anneal at 1100°F (593°C) minimum for one hour at temperature for each inch of thickness or some similar treatment at somewhat lower temperatures for longer times. Stress relief is usually effected by insulating the vessel to the appropriate height and heating with gas/oil burners. Carbon steel vessels fabricated before June, 1964 were required by the code to undergo

stress relief if the wall thickness exceeded 1" for A212 vessels or 1 1/4" for A285 vessels. In many vessels, the transition from thicknesses requiring stress relief to those that do not occurs at or near the cooking zone transition. Consequently, many vessels are stress relieved up to some elevation in the impregnation zone, but not above. Some vessels were stress relieved at the request of the mill purchasing the vessel. Of the 103 carbon steel vessels in kraft pulping service for which stress relief conditions are known, 19 have had no stress relief (usually small sawdust digesters), 47 have been partly stress relieved, and 37 have been completely stress relieved, flange-to-flange. Impregnation vessels are usually not stress relieved because of their small size and relatively thin walls, although some mills have specified stress relief of these small vessels.

After the vessel is fabricated and the stress relief procedures completed, the digester internals are installed. The central distribution pipe is installed with triangular gusset plates welded to the vessel shell supporting the concentric pipes. The top separator is also installed. The screens and dummy plates above the screens are also attached after the stress relief treatment, usually by manual stick welding to the shell.

As required by the ASME Code, all vessels are hydrotested after construction to demonstrate the integrity of the vessel before service. Since the design pressure of virtually all Kamyr digesters is 165 psi at the top (and higher by the hydraulic head at the bottom of the vessel), the typical overpressure used in the hydrotest is 250 psig at the top of the vessel.

#### Cracking Characteristics in Kamyr Continuous Digesters

The resistance to weld cracking exhibited by the various Kamyr digesters varies widely, not only in severity, but also in crack morphology.

Some vessels have exhibited no cracking of any sort, whereas other vessels have experienced through-wall cracking and even vessel failure. Some cracked vessels exhibit long, interconnecting longitudinal\* cracks in the heat-affected zone, while other vessels exhibit numerous long transverse\* cracks. In some vessels, cracking is restricted entirely to the weld metal; in others, the heat-affected zone is susceptible.

The objectives of this subsection are to catalog the various types of cracking reported by the various mills, and to give some appreciation for the prevalence of a specific type of cracking. The attempt to correlate this cracking experience with digester operation or fabrication is reserved for subsequent subsections. The TAPPI Task Group settled on a system for grading severity of cracking in vessels as follows:

Grade A - Severe Cracking;  $\geq 1/4"$  deep,  $> 2"$  long

Grade B - Moderate Cracking;  $1/16" \leq \text{depth} < 1/4"$

Grade C - Incipient Cracking;  $< 1/16"$  deep

Grade D - No Significant Cracking

This grading system is preserved in this report.

As of January 1983, 107 Kamyr vessels involved in alkaline pulping had been inspected, with reports forwarded to the TAPPI Task Group or to the Institute of Paper Chemistry. Most of these reports are documented, although some were made verbally by credible respondents. About two-thirds of the status reports on digester inspection are considered up-to-date. The remaining one-third are considered incomplete because of infrequent inspections or a failure

---

\*Longitudinal cracks run parallel to the direction of the weld pass. Transverse cracks are perpendicular to the weld pass.

(or refusal) to share recent inspection information. In some cases, vessels have been retired from operation and are excluded from this survey. In other cases, vessels have been significantly altered and are now in operation in new circumstances as, for example, in the use of an old vessel in a two-vessel retrofit. In this survey, impregnation vessels and digesters in two-vessel mills are treated as a single vessel. In many cases, the details of mill operation have changed significantly in past years, and current information may not be representative of past operation. An effort was made to use information appropriate to the period of cracking where a choice was possible. In spite of these caveats regarding the veracity of the original data, some interesting trends do emerge from the cracking statistics.

#### Cracking Statistics

The number of vessels exhibiting cracking appropriate to Grades A, B, C, D is summarized below, excluding nozzle cracking and stitch weld cracking:

TABLE III  
CRACKING STATISTICS

Condition	Cracking Grade			
	A	B	C	D
Stress relieved in impregnation zone	7	2	5	23
Not stress relieved in all of impregnation zone	33	12	7	18
Total	<u>40</u>	<u>14</u>	<u>12</u>	<u>41</u>

Forty percent of the digesters have exhibited cracking at or beyond the 1/4" corrosion allowance, thereby necessitating repairs. Of these severely cracked vessels, 83% were not stress relieved in the impregnation zone area. Forty percent of the vessels have exhibited no significant cracking in weldments,

including 18 vessels which were not stress relieved. Two thirds of the non-stress-relieved vessels have exhibited cracking of A or B severity.

#### Distribution of Cracking

At one mill or another, cracks of "A" severity were observed in each of the welds in the impregnation zone of the typical Kamyr digester, including horizontal, vertical, transition, and top head welds. In addition, cracks were frequently observed in the welds which joined the downcomer support gusset plate to the shell wall. Many mills reported extensive cracking in and around nozzles in the upper regions of the vessel. Many vessels, including those otherwise immune to cracking, exhibited cracking in stitch welds attaching dummy plates and screens to the vessel wall. In some cases, downcomer pipes were cracked in welds, as well. Localized corrosion in the form of erosion corrosion gouges were common in the cone wall. Corrosion of the heat-affected zones of welds was also commonly reported.

#### Crack Morphology

The morphology of cracking varied greatly from mill to mill. The most severe cracking from the standpoint of digester reliability was relatively deep, contiguous cracking in the heat-affected zones (HAZ) of girth welds. This longitudinal cracking mode was occasionally found to crack 90% of the circumference of a weld to a depth of 1/2" or more. Severe cracking was also observed in the HAZ of the fillet welds attaching the downcomer pipe support to the shell. Longitudinal cracking was also observed in the weld metal itself, although the penetration of this type of cracking seemed to be less than that observed in the HAZ area. Short transverse and longitudinal cracks in the weld metal were often very shallow (~ 1/16"-1/8"), giving the appearance of crazing. In at least two

mills, transverse cracks initiated at the HAZ had propagated well into the base metal of the plates adjacent to the weld, producing cracks three to four inches long and 1/2" deep. Cracks observed at nozzles were frequently observed to radiate outward from the nozzle weld (transverse cracking).

Most reports of cracking of weldments described several varieties of cracks occurring simultaneously, usually with differing severity. For example, severe longitudinal cracking of girth welds might be accompanied by shallow transverse cracking of the weld metal.

#### Cracking in Base Metal

The carbon steel of the plate material was virtually immune to cracking at sites removed from any weld, although examination of the broad expanse of plate area has not been especially careful. Transverse cracks can penetrate into the base metal, well removed from any influence of microstructural changes associated with the weldment. Cracks initiated at the fillet welds attaching the downcomer pipe support have also penetrated the shell, indicating growth through base metal located some distance from the heat-affected zone of the weld. In one case, the small region of A285-C-MOD base metal between the attachment of the cone and the adjacent girth weld exhibited shallow cracking. The effect of metallurgical changes on this region due to the heat input from several adjacent welds is not clear.

#### Cracking at the Cone Transition Weld

The cone transition weld is especially susceptible to cracking in continuous digesters. The lower cone transition weld is the weld at which the Pine Hill vessel ruptured, although all of the welds in the impregnation zone were cracked in that vessel. In the sixteen vessels containing cracks deeper than



1/2", ten exhibited these deep cracks in the upper or lower cone transition welds. Most of these welds were cracked to 1/2" deep in the HAZ region, but at least one mill reported 1/2"-deep transverse cracks at the lower cone transition weld. In three cases, Grade A cracks were found at the lower cone transition weld and the adjacent vertical welds in the cone, but no cracking was found elsewhere in the vessel.

#### Deep Cracking (> 1/2")

Severe cracking -- deeper than 1/2" -- was observed in sixteen continuous digesters, thirteen of which had not been stress relieved at the affected weld. As mentioned above, nine of these cases involved cracking at the welds associated with the cone transitions, mostly the lower transition. Two of the deep cracks were associated with growth of cracks which initiated at the downcomer support and propagated into the shell. Two of the sixteen cracks deeper than 1/2" were in girth welds not at the cone and two cracks deeper than 1/2" were found in vertical welds. In at least five cases, cracks either penetrated the shell or were chased through the shell wall in an attempt to grind out the crack before repair welding. Two of these through-wall cracks were reported to be 18" and 12" long.

#### Impregnation Vessel Versus Digester Cracking

In two vessel systems, the impregnation vessel (IV) is generally more susceptible to cracking than the second vessel -- the actual digester. Several cases have been cited where welds in impregnation vessels cracked, with no cracking reported in the digester proper. This does not imply that second vessel digesters are immune to cracking, however. At one mill, a crack initiated at the downcomer support weld and penetrated the vessel wall in two years of operation, but the deepest crack in the impregnation vessel was only 0.35" deep.

### Cracking Outside of the Impregnation Zone

Virtually all of the cracking occurring in continuous digesters has occurred in the impregnation zone of the vessels. However, there have been a few reports of cracking in locations at or below the cooking zone. One Canadian mill reported cracking in virtually all of the girth welds in the entire vessel. In another case, cracks less than 1/4" deep were found at the bottom of pits in the cook/extraction zone by grinding through the pits and conducting wet fluorescent magnetic particle (WFMT) inspections. A third mill reported cracking in the stress relieved portion of the digester vessel -- presumably in the zone below the cooking region. A fourth mill reported 1/2"-deep cracks in a transition weld in the stress relieved area -- presumably also below the impregnation zone.

### Nozzle Cracking

Many of the mills providing inspection reports describe significant cracking of various nozzles in the impregnation zones of their vessels. In virtually every case, the most severe nozzle cracks were oriented predominantly transverse to the nozzle weld, emanating radially outward from the axis of the nozzle. With this orientation, nozzle cracking is unlikely to lead to vessel failure similar to that observed at Pine Hill, provided a regimen of routine inspections is maintained.

The influence of fatigue stresses on nozzle cracking may be significant. Stresses induced by pipe flexure could be transmitted to the nozzle welds and promote crack initiation. The influence of these cyclic stresses on nozzle cracking is, at present, unknown.

### Vertical Welds Vs. Horizontal Welds

Vertical welds in the impregnation zone are generally less affected by cracking than the horizontal girth welds, although many exceptions have been reported. In many instances, the severity of cracking is similar for horizontal welds and adjacent vertical welds. At one mill, for example, both vertical and horizontal welds in an impregnation vessel exhibited Grade A cracking, but the cracks in the vertical welds were three times as deep as those in the girth welds. In other cases, the reverse is true. In at least eleven instances, the vertical welds in vessels were reported to be as severely cracked, or more so, as the adjacent girth welds.

### Average Crack Penetration

Crude estimates of average crack growth rates can be obtained from reports of inspection and reinspection data, where cracks initiated in the intervening period. In this analysis, the actual growth rate may be seriously underestimated since the incubation period preceding crack growth is uncertain. Carried to extreme, for example, all of the growth observed in a yearly inspection could occur on the day before an annual shutdown, and the actual growth rate would be 350 times higher than the average calculated growth rate. There is the additional possibility that growth rates may be too high because all cracks were not discovered during the initial inspection. In spite of these uncertainties, some of the higher crack penetrations reported are listed below:

TABLE IV  
PENETRATIONS

Mill	Location	Growth	Time
002	Downcomer support	1.1"	24 mo.
022	Downcomer support	1.1"	18 mo.
071	Lower cone girth	0.5"	12 mo.
087	Lower cone transition	0.5"	6 mo.
120	Transverse girth welds	0.6"	24 mo.
143	Vertical weld	0.75"	8 mo.
012	Repair weld	0.09	5 mo.
135	IV girth	0.25	14 mo.

#### Onset of Cracking

In several instances, careful NDE studies revealed that cracking occurred within the time period between inspections; i.e., after long periods without cracking, sudden crack initiation and growth was possible. In mill 116, for example, no cracks were detected after fifteen years of continuous operation, yet cracks 1/4" deep were observed after 16 months of further operation.

#### Metallography

Although most mills have merely removed cracks by grinding or welding and returned vessels to service, some mills have conducted more detailed failure analyses. Several mills have arranged for metallurgical consultants to take boat samples from affected weld areas, to assess the path of cracking through the microstructure, and to assess the possible role of metallurgical structure or cracking. Several interesting observations have resulted from these investigations.

In several separate studies, the composition, hardness, and microstructure of several weldments were determined in cracked vessels. The composition of several weld metals and a base metal are given in Table V. The welds and base metals have typical compositions, with the exception of a slightly high Si content in the one base metal. The hardnesses at the weldments are also shown in Table II, and these too are unremarkable. The high hardness of the HAZ is evidence of a martensitic structure formed at the junction with the weld metal. Limited metallography failed to reveal any unusual microstructural features of the welds.

Crack initiation was found in several of the metallographic studies reported in confidence. Cracks typically initiated at the bottom of minute corrosion pits located in the HAZ of the welds, or in the weld metal itself. Cracks grew along ferrite-ferrite boundaries in the weld metal or along acicular ferrite boundaries in the metastable structure in the HAZ. There was some evidence of growth by preferential dissolution of ferrite in pearlite in one instance of crack growth through the base metal.

#### Nondestructive Examination

Considerable effort was expended by the TAPPI Task Group in an attempt to determine optimum NDE methods for evaluating cracking. Eventually, the Task Group recommended internal inspection by wet fluorescent magnetic particle methods (WFMT) after careful grinding of the weld surface. Different orientations of the magnetizing yoke were effective in identifying transverse and longitudinal cracks. The use of qualified inspectors was also emphasized.

Alternative inspection methods were also used by some mills as the optimum inspection method was being sought, including ultrasonic testing (UT) by

TABLE V  
COMPOSITION AND PROPERTIES OF WELDMENTS

Weld	C	Mn	Cu	Cr	Ni	Si	Mo	P	S	Al
E7018 #1	0.06	0.90	0.06	0.05	0.04	0.26	0.01	--	--	--
E7018 #2	0.09	0.62	0.07	0.04	0.03	0.24	--	0.012	0.020	<0.01
Base Metal (A516)	0.30	0.88	0.05	0.02	0.02	0.35	--	0.011	0.020	<0.01
ASTM Std. (A516)	0.31 max	0.85- 1.25	--	--	--	0.15- 0.30	--	<0.035	<0.04	--
E70TG (Electrogas)	0.09	1.35	0.07	0.07	1.10	0.50	0.02	--	--	--

Hardness (R <sub>B</sub> )			
Weld	Base	HAZ	
E7018 #1 (Stress relieved)	86	68*	69*
E7018 #2 (As-welded)	93-99	82-87**	99-107**

\* A-285C  
\*\* A-516-70

shear wave reflection from the outside of the vessel, dry fluorescent magnetic particle testing, and acoustic emission (AE) testing. The success of these alternative NDE measures was generally lower than that of the WFMT method.

UT conducted with the vessel still hot is an attractive method of inspection because of the minimal preparation and downtime associated with the method. However, it appears that the resolution of the method may only allow detection of cracks deeper than 1/4" on the interior weld surface. In at least four cases, hot UT methods failed to indicate cracks as deep as 1/4"; these were later revealed by WFMT methods. In at least three cases, no evidence of cracking was found by either hot UT or by WFMT methods. In one case, 1/4"-deep cracks detected by hot UT were confirmed by subsequent WFMT. Consequently, hot UT seems appropriate only as a tool for detecting gross cracking without vessel downtime.

Acoustic emission testing is also attractive because it is a relatively noninvasive NDE method that does not require extensive downtime on the vessel. In this method, the vessel is instrumented with sensors capable of detecting the acoustic emissions that accompany an abrupt crack advance event. The vessel is pressurized to a pressure 10% above the previous high pressure value while the detector array is monitored for evidence of crack advance. Acoustic emission sites are then located by triangulation based on time of flight analysis of the sound waves emitted.

Although AE methods would be much less time consuming than WFMT, several mills have reported an inability to detect relatively large cracks using this method. In many cases, there was acceptable correlation between AE and WFMT examinations, but five mills reported detecting emission sources that could

not be confirmed by WFMT, or failing to detect by AE sources known to exist from WFMT. One respondent complained of poor lateral resolution of cracking locations (+ 7 ft x + 3 ft). Grading of AE cracks by intensity of emission is still an evolving technology. Initially, one AE inspector recommended action only for Grade A and B sources, but recently changed its recommendation to include more detailed inspection for Grade C sources (the minimum detectable source) as well. Although some mills have installed permanent AE apparatus and are relying on this approach for routine vessel inspection (with the consent of their insurer), some questions remain regarding the conservatism of this NDE approach.

Noted in passing are some reported events which occurred during magnetic particle inspections. In one case, dry fluorescent magnetic particle testing (DFMT) was first used, followed by WFMT. The WFMT revealed significant cracks that had not been detected by DFMT methods. In another case, shallow transverse WFMT indications occurred in the weld after a day of "aging" the freshly ground surface in air. These recurrent indications could be induced repeatedly by grinding and "aging" sequences.

### Summary

Nearly every conceivable crack morphology has been reported in continuous digester weldments. Most cracking is restricted to the non-stress-relieved impregnation zone of Kamyr digesters. The most serious cracking has occurred in the HAZ of girth welds in transition areas and downcomer support welds, although through-wall cracking has also been reported in vertical welds. High crack growth rates have been inferred from repeated NDE evaluations of welds.

### DIGESTER CRACKING VERSUS FABRICATION VARIABLES

Since some vessels have cracked whereas others have not, an attempt was made to relate cracking susceptibility to the conditions used in fabrication of



the digester vessels. Through the responses of the mills and the cooperation of Kamyr, some of the general characteristics of each vessel -- such as alloys used, stress relief treatment, size, etc. -- were determined for correlation with cracking susceptibility. A more detailed scrutiny was made of the six specific mills selected for special attention. For these latter mills, detailed vessel fabrication procedures were obtained from the mill, Kamyr, Inc. or the mechanical erector, so cracking susceptibility at any weld could be related to exact welding procedure for that weld. As discussed earlier, the field construction notes must be consulted to ensure that the actual procedures are identified since erection drawings may have been modified in the field.

There is a strong correlation between immunity from cracking at any weld and the stress relief of that weld. Forty-five of seventy vessels\* without stress relief of the welds in the impregnation zone exhibited Grade A or B cracking in those welds. On the other hand, only nine of thirty-seven vessels stress relieved in the impregnation zone exhibited grade A or B cracks, whereas twenty-three have shown no cracking susceptibility at all. Apparently, stress relieving of the impregnation zone reduces the probability of A or B cracking from a 70% probability down to 25%.

In contrast to what might be expected, there is some difference between vessels which were partially stress relieved (below a certain elevation) and vessels which received no postweld heat treatment at all. For example, of the 45 vessels with Grade A or B cracking, only five received no stress relief; of the 18 vessels with no cracking (Grade D performance), eleven received no

---

\*Two-vessel systems are taken as a single vessel and are combined as being cracked if either the impregnation vessel or the digester vessel exhibited cracking in non-stress-relieved welds.

weld heat treatment. These statistics are puzzling until it is realized that the the vessels receiving no postweld heat treatment are smaller than those receiving a partial treatment, and size appears to affect cracking susceptibility.

There is also an apparent correlation between mechanical erector and cracking susceptibility which may or may not be significant. Of the 44 vessels showing A or B cracking, all but one were constructed by one company. On the other hand, 36 of 46 vessels showing no cracking were constructed by this same company. The remaining ten vessels were constructed by seven different erectors. Again, these statistics may be misleading, in that the principal mechanical fabricator is usually involved in manufacturing large and small vessels, whereas the other fabricators concentrate on construction of the smaller, less susceptible digester vessels.

The effect of size and throughput on cracking susceptibility is shown schematically in Fig. 23 and 24. The preponderance of immunity (type D) is seen for vessels with small throughput, and the preponderance of susceptibility (type A) is seen in vessels with large throughput. Moreover, for those sixteen vessels exhibiting deep cracking ( $> 1/2$ " deep), all but three were larger than 600 air dry tons/day. Since actual vessel size (diameter) is not directly proportional to throughput, some of the SCC data has been replotted in Fig. 24 on the basis of actual vessel diameter in the impregnation zone. Using this criterion, larger vessels appear to be slightly more susceptible to severe (type A or B) cracking than smaller vessels. However, impregnation vessels are relatively small in diameter, yet these vessels have exhibited severe cracking.

There appears to be little correlation between date of construction and SCC susceptibility, as shown in Fig. 25. Most of the vessels were built in the

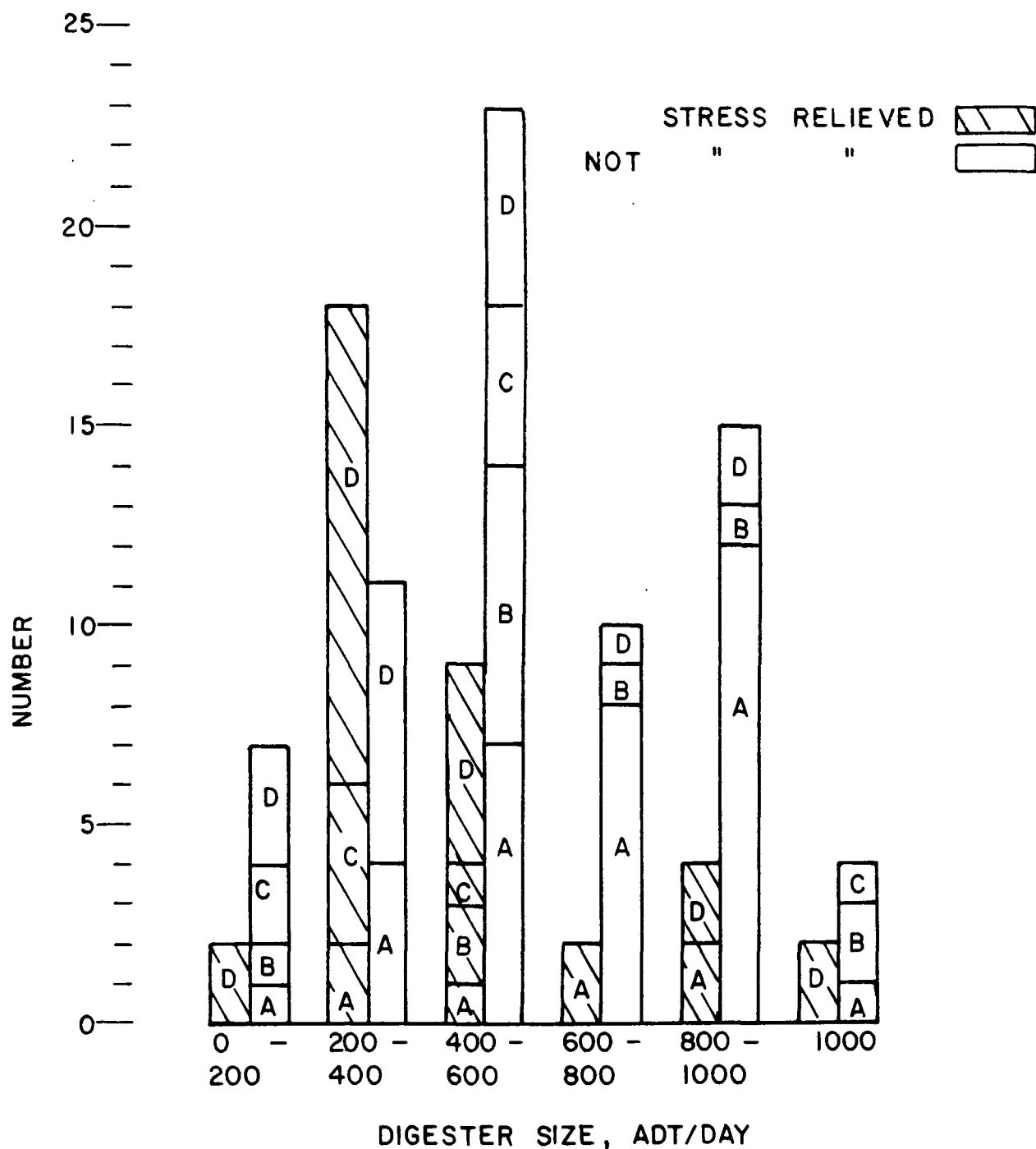


Figure 23. Histogram showing the effect of digester size (in ADT/day) versus cracking severity. Severe cracking  $> 1/4"$  is Grade A; immunity from cracking is Grade D.

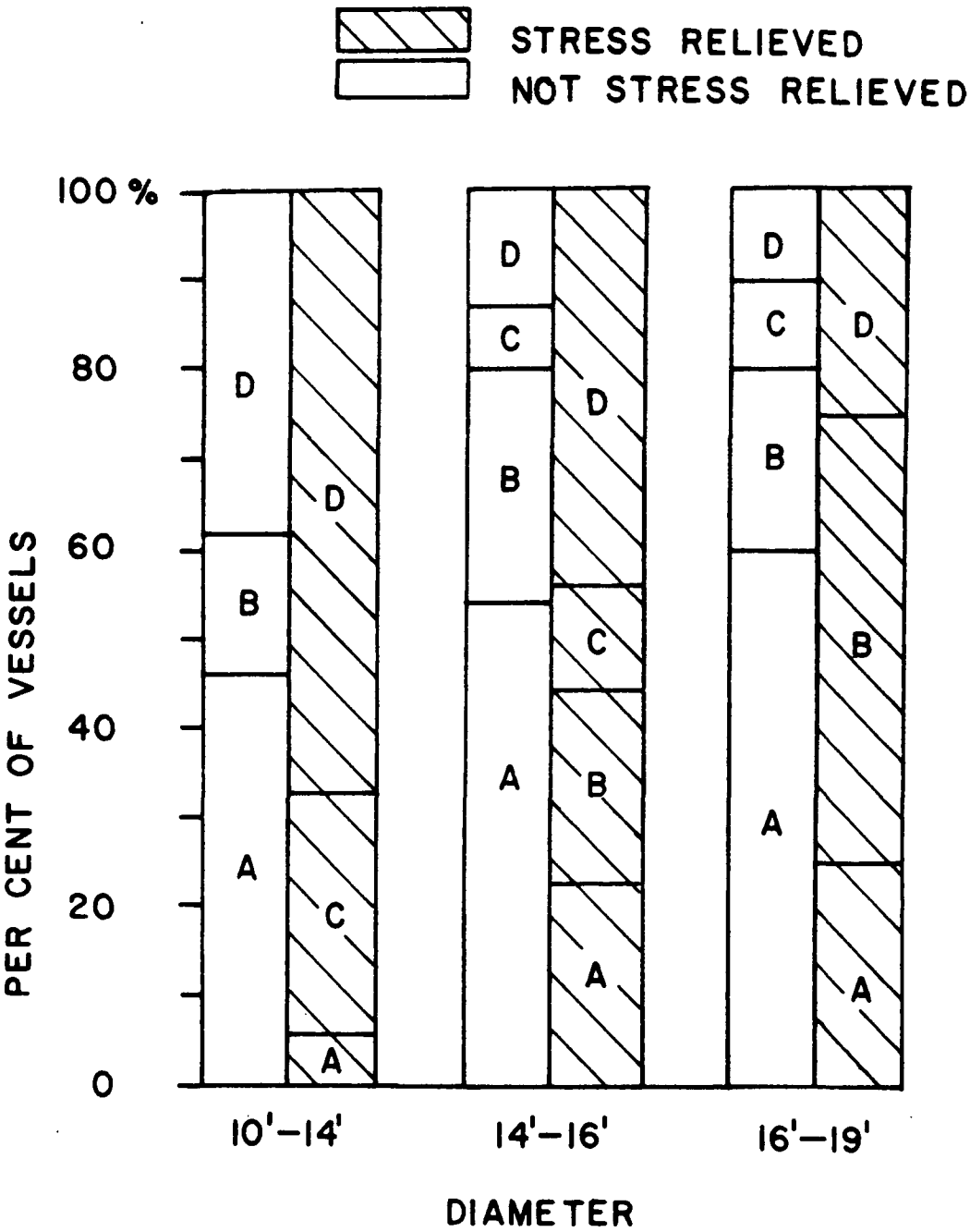


Figure 24. Histogram showing the interrelation between vessel size, stress relief treatment, and cracking susceptibility. A = most severe; D = no cracking.

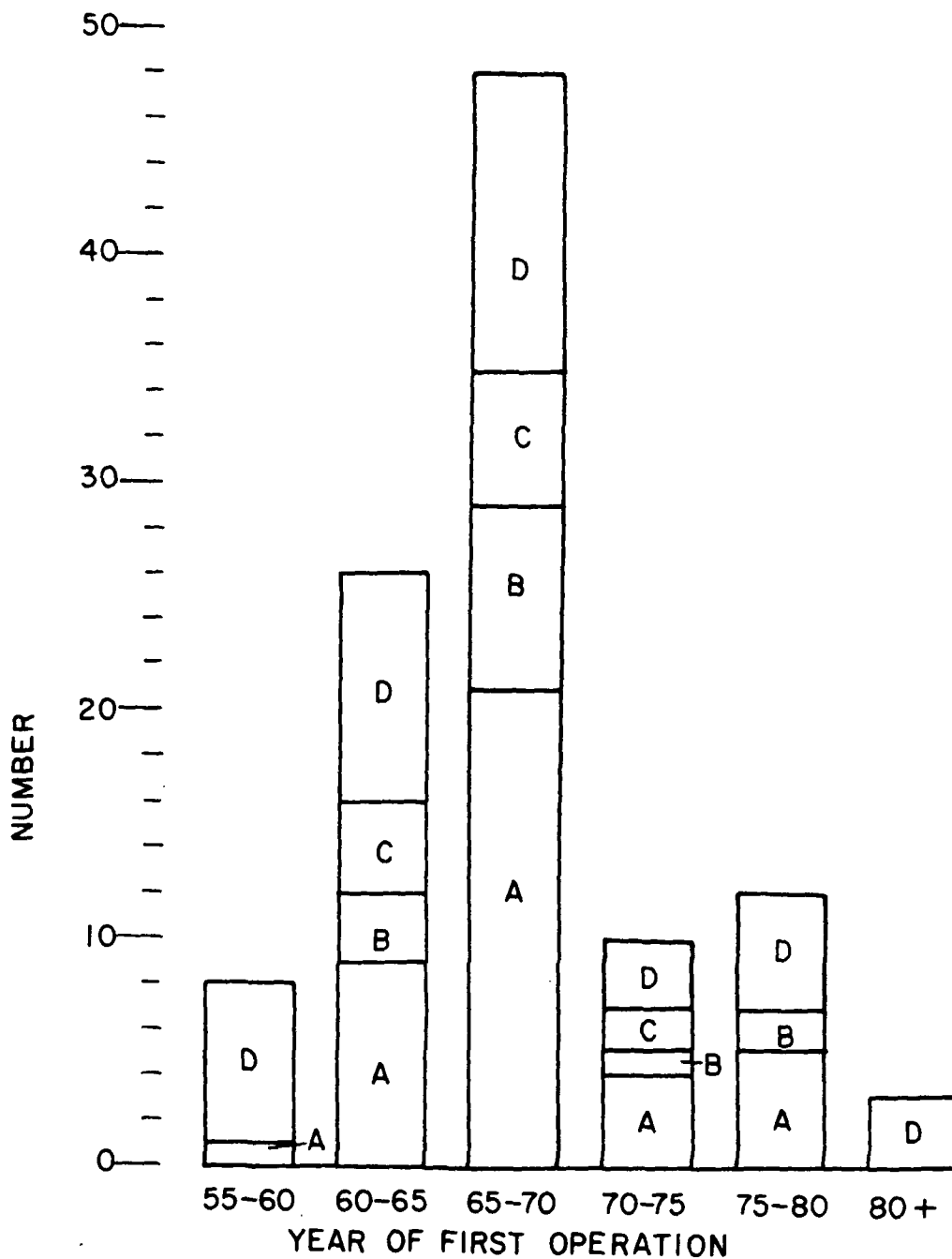


Figure 25. Histogram showing approximate date of construction versus cracking susceptibility. A = severe cracking; D = no cracking.

1960's. The distribution of A cracking vessels is about the same as the D, noncracking vessels. As discussed above, the first vessels built were completely stress relieved and immunity from cracking predominates, as is the case for vessels coming into service since the Pine Hill failure.

As shown in Fig. 26, the four steels used in vessel fabrication differ little in their susceptibility to SCC. The A516 steel is slightly more susceptible than the remaining steels, and the A285 steel is slightly less susceptible, based on results for non-stress-relieved vessels. All eight A516 vessels that were stress-relieved before service have escaped cracking. The histogram for A212 steel represents only four vessels, two stress relieved and two not stress-relieved.

To evaluate the effects of welding variables on cracking of specific weldments, the construction notes were obtained for the six mills involved in the on-site survey activity, for correlation with cracking records for each of the welds in the impregnation zone of each vessel. Of the seven\* vessels considered, three had been immune to cracking and four had exhibited Grade A cracking in some of the welds. One of the vessels was an impregnation vessel; the balance were digesters. The welding procedures for each weld are shown schematically in Fig. 27 to 33. All three types of welds commonly used in digester vessel manufacture were present in the welds comprising this sample. None of these vessels had been stress relieved in the impregnation zone.

There appears to be no strong correlation between welding procedure and cracking susceptibility based on this sample, with the exception that electrogas

---

\*One mill had two digesters.

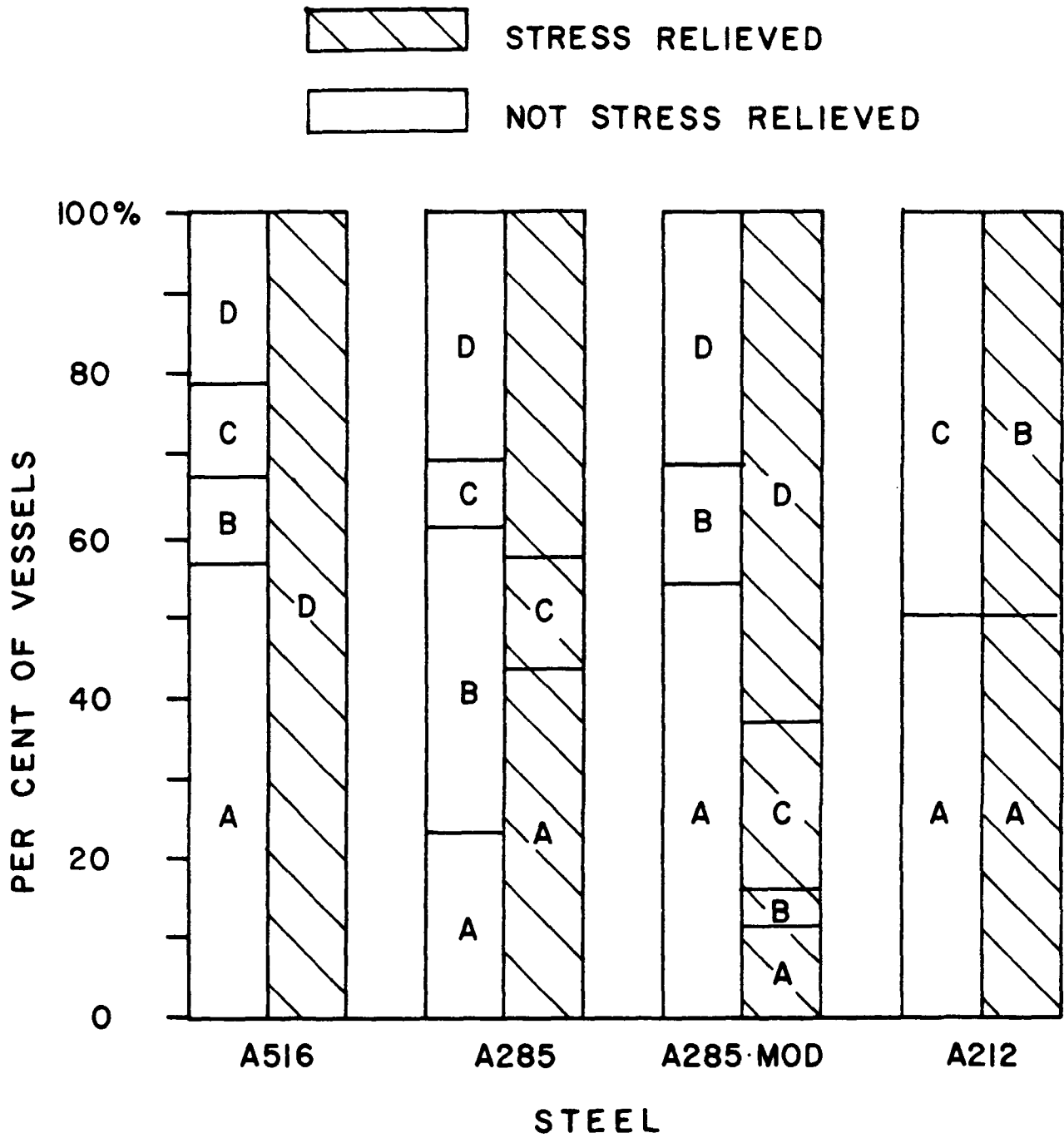
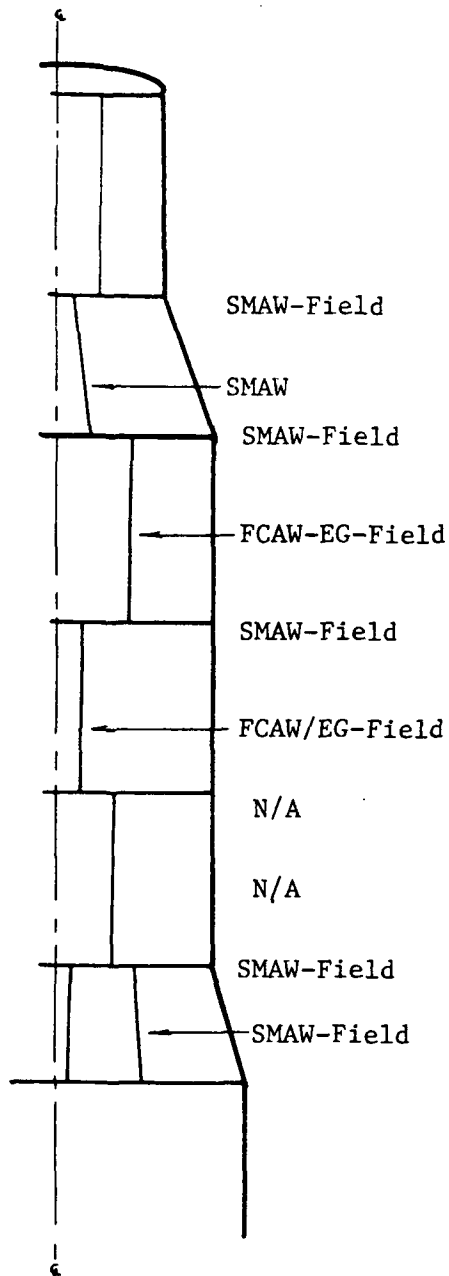


Figure 26. Histogram showing materials effects versus base metal used in the impregnation zone.



Mill 60 - No Cracking

Base metal - A516-70

SMAW - E7018

FCAW-EG - McKay SA66, two  
pass, manual root pass

Figure 27. Welding procedure versus cracking record for mill 60.



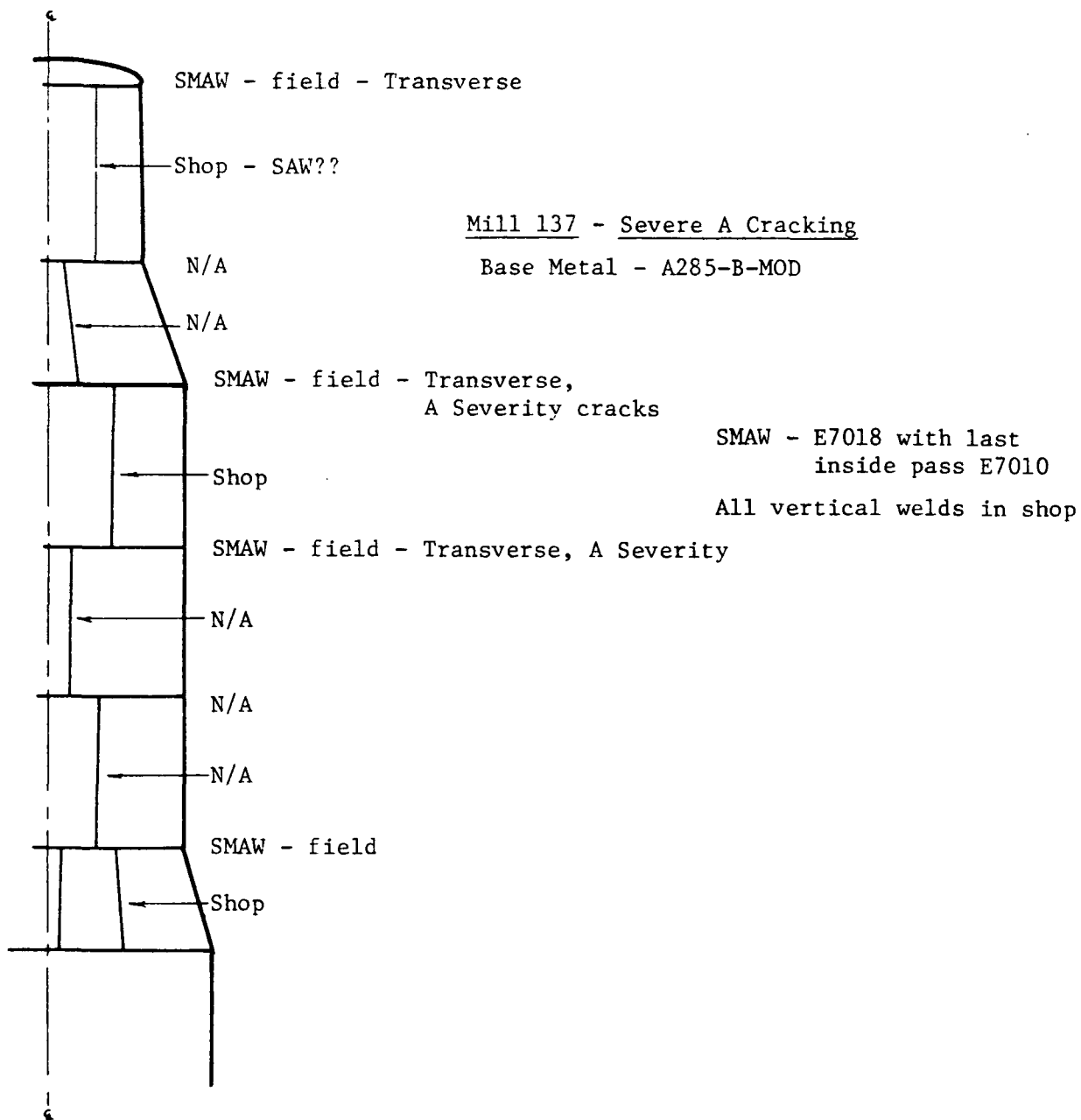


Figure 28. Welding procedures versus cracking record for mill 137.

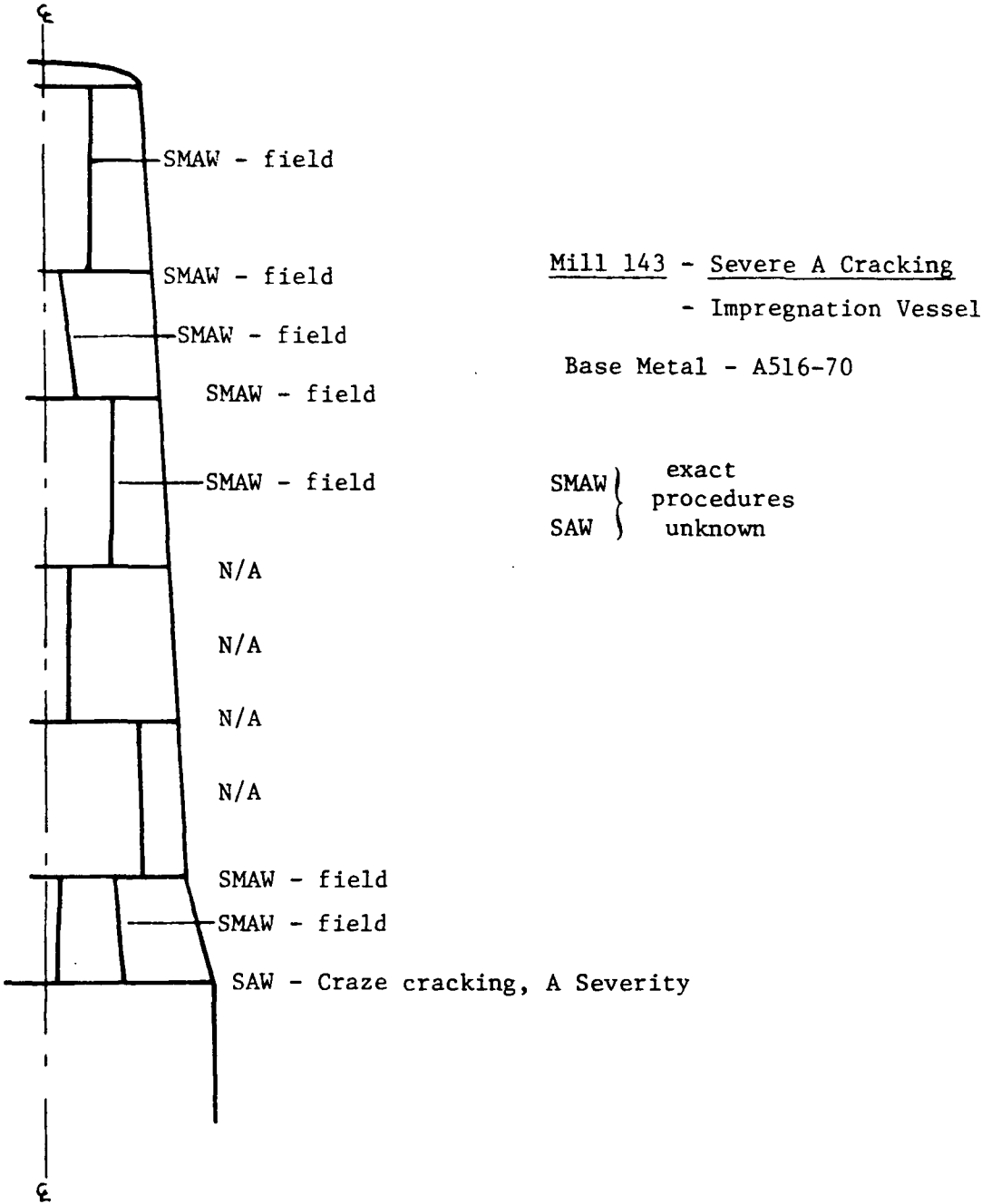


Figure 29. Welding procedures versus cracking record for mill 143.

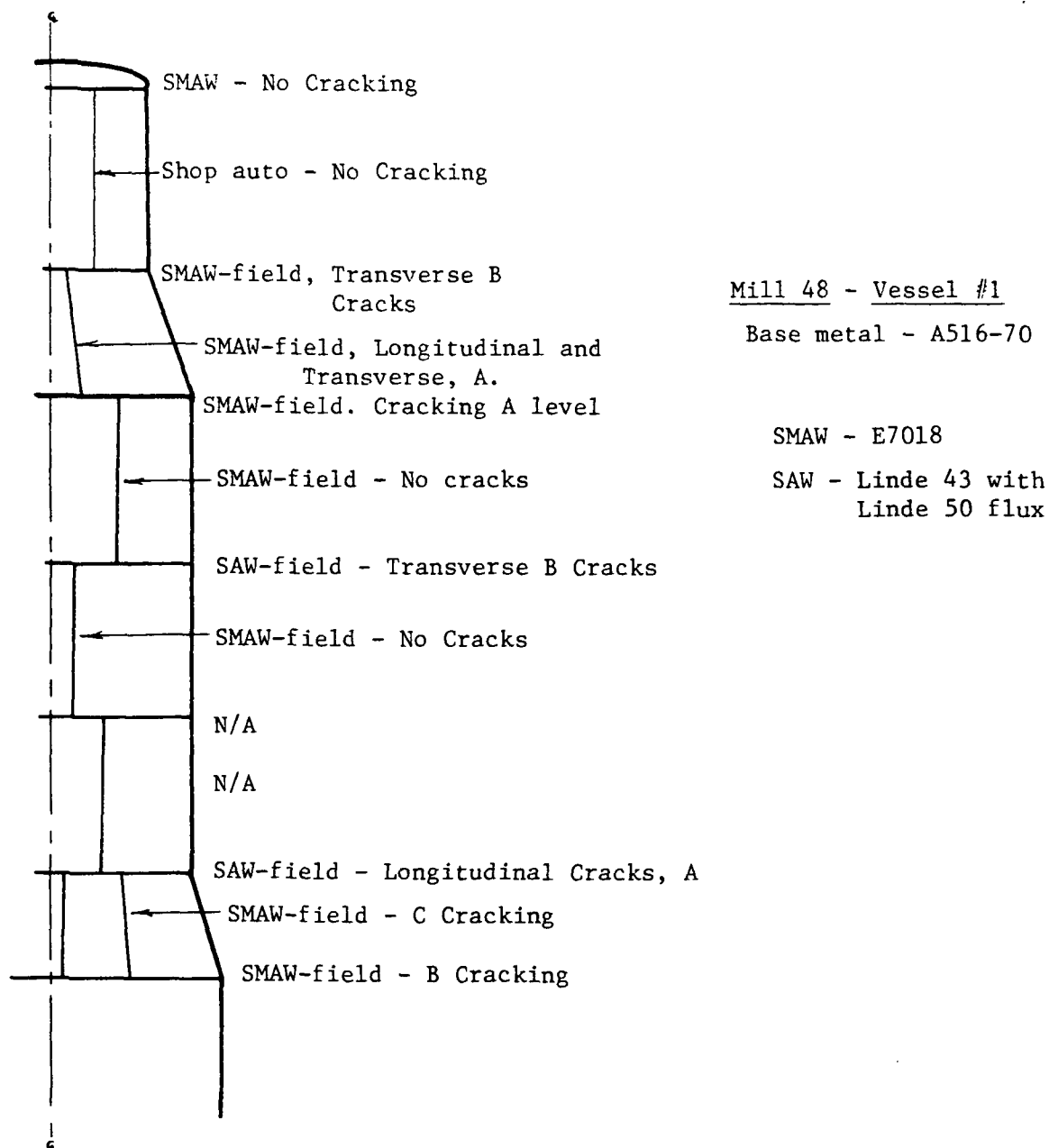


Figure 30. Welding procedures versus cracking record for mill 48-1.

Mill 39 - Vessel 2

Base Metal - A285-C-MOL

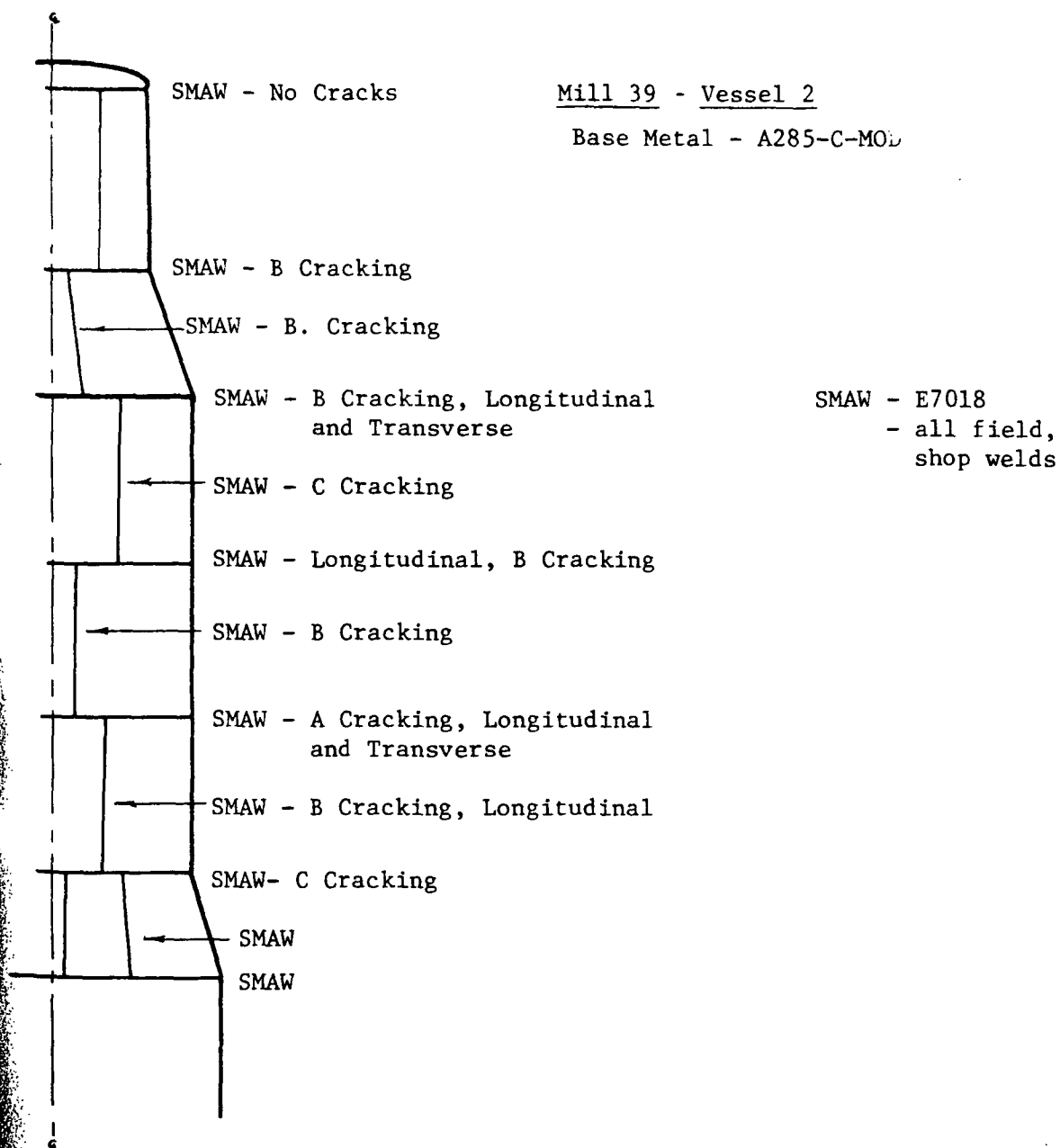


Figure 31. Welding procedures versus cracking record for mill 39.

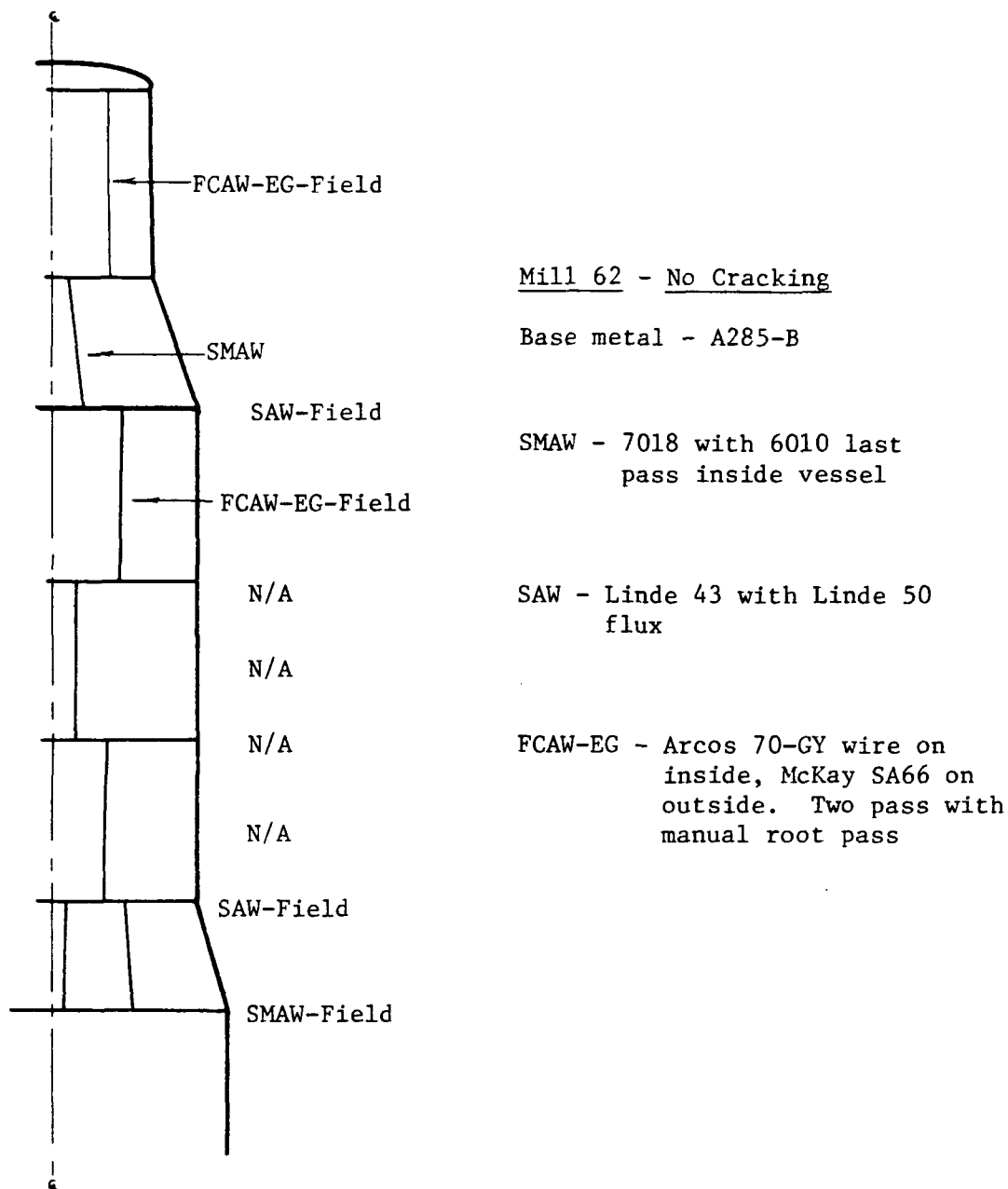
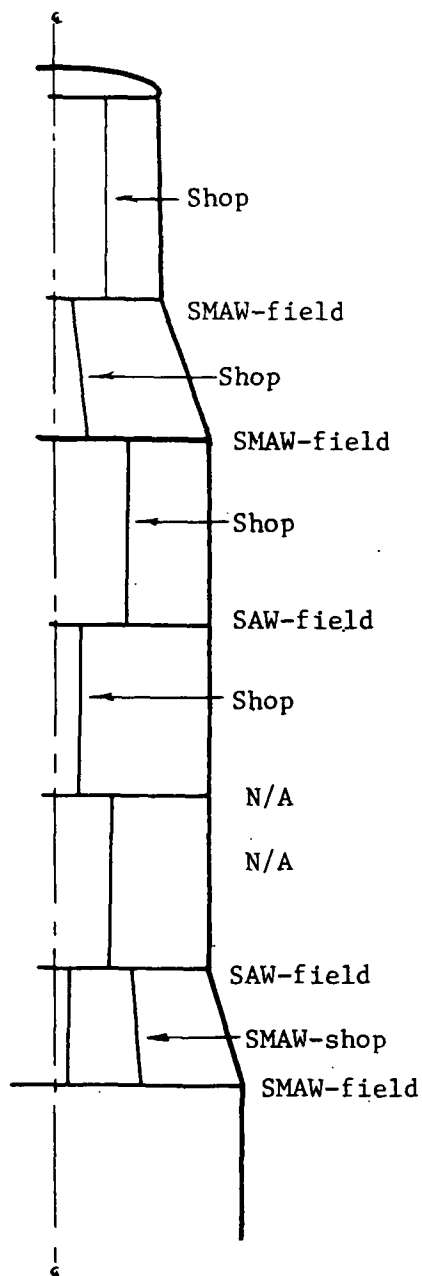


Figure 32. Welding procedures versus cracking for mill 62.



Mill 110 - No Cracking

Base metal - A285-C-MOD

SMAW - E7018, with E6010 last  
pass inside vessel

SAW - Linde 50 metal with  
Linde 50 flux

Figure 33. Welding procedures versus cracking record for mill 110.

welds did not exhibit any evidence of cracking. Some noteworthy points are listed below:

- (i) Cracking occurred in 7018 vertical and girth welds made with the SMAW process (mill 48).
- (ii) Two vessels with low-silicon, E6010 overlays on internal hand welds did not exhibit cracking (mills 62, 110), but one mill with E7010 overlays on the weld exhibited Class A cracking (mill 137).
- (iii) In one case, shop submerged arc welds did not crack, whereas adjacent SAW welds showed A type cracking (mill 137). In another case, only a submerged arc weld cracked in a vessel otherwise welded with E7018 SMAW procedures (mill 143 IV). In mill 48, both SMAW and SAW welds exhibited cracking of A severity.
- (iv) SMAW welds produced in virtually the same fashion, to the same welding specification, showed different cracking propensities. For example, the SMAW welds in vessels 39, 110, and 62 were done according to the same procedure (heat input, electrode size, etc.), yet only the welds in vessel 39 exhibited cracking.
- (v) SAW welds produced in virtually the same fashion, to the same welding specification, showed different cracking propensities in different vessels. For example, SAW welds in vessel 48 exhibited significant cracking, whereas the SAW welds in vessel 110, made with the same procedure, did not crack at all.
- (vi) There appears to be no correlation between welding procedure and crack morphology (longitudinal or transverse).
- (vii) Electrode gas welds did not exhibit cracking in vessels 110 and 62. However, no electrode gas welds were present in the other vessels

where cracking of SAW and SMAW welds had occurred. Electrode gas welds are known to crack in other vessels not included in the present sample.

Based on the above observations, there appears to be no correlation between the cracking susceptibility of a given weld and the welding procedure used to fabricate that weld.

Aside from good correlations between cracking susceptibility and digester throughput and stress relief treatment, it appears that the fabrication variables (that can still be identified long after vessel construction) do not have a significant effect on the likelihood of cracking in a given vessel. However, many variables in fabrication cannot be obtained many years after vessel construction. The skill and diligence of the welding crew, the sequence of welding operations, conditions of weld heat input -- those and many other potentially important variables are lost from view. If these fabrication variables have a role in the code that controls cracking susceptibility, it is unlikely that the code will ever be deciphered.

#### DIGESTER CRACKING VERSUS OPERATION

Since the obvious fabrication variables do not seem to affect digester cracking significantly, is the difference between immune and susceptible vessels caused by differences in operating procedures? To examine this question, data were analyzed from two sources. First, the updated version of the TAPPI Task Group questionnaire requested rudimentary information about plant operations -- white liquor composition, acid cleaning practices, wood species pulped -- and many mills provided this information. A second source of information was the survey questionnaire filled out at each of the six mills selected for an on-site visit. The same detailed questionnaire (included as an Appendix) was submitted



to three susceptible and three nonsusceptible mills with the hope of trying to identify differences between the two types of mills. In some cases, personnel from the selected mills balked at the length and detail of this latter survey, so this survey is not as complete as desired. A third source of information -- chemical and electrochemical characterizations of cooking liquors at the six mill sites -- is reserved for discussion in a subsequent section.

In February 1981, the TAPPI Task Group requested in its questionnaire some fundamental details of pulping processes at each mill. Many of the mills responded by providing information regarding liquor chemistries, wood species pulped, and acid cleaning practices. A renewed request for information as part of this DCRC program at the Institute brought additional responses, together with new information on inspection results. With the updated data base, an attempt to correlate cracking susceptibility with operation was made.

#### Acid Cleaning

The similarity of kraft pulping processes in North America, and the widespread occurrence of cracking combine to confound identification of pulping practices that promote cracking. For example, virtually every mill operating a continuous digester and responding to the questionnaire finds it convenient to clean internal screens by acid cleaning, i.e., circulating an inhibited hot, dilute acid solution through the plugged screens. Of the 60 vessels in North America for which a response is available, only 4 are not acid cleaned.

The fifty-six vessels which are cleaned with acid are typically exposed to a similar cleaning procedure. After the vessel is washed and filled with water to the cooking screen level, inhibited acid is added at a pump suction to raise the acid concentration to about 3-5%. The dilute acid mixture is heated

and recirculated through the various screens until the acid residual reaches a prescribed level. The tank is then drained, perhaps rinsed with water, and passivated by exposure to white liquor. In all but two responses, hydrochloric/muriatic acid is described as the acid used; sulfamic and formic acids are used in the two exceptional cases. There is no correlation between cracking susceptibility and acid used in acid cleaning. Too few responses were obtained regarding the inhibitor used to evaluate the possible role of inhibitors on SCC. Frequent acid cleaning also does not induce cracking in digester vessels. For example, two non-stress-relieved vessels have been cleaned every 3-4 months without developing cracks during operation for more than a decade. Conversely, severe cracking has been reported for vessel 71, which is acid cleaned only every three years.

Some exceptional circumstances involving acid cleaning practices are noteworthy. Four of the vessels in the North American survey are not acid cleaned. These four vessels have not shown any evidence of cracking in shell welds. All four vessels have been stress relieved, however, and would be expected to be less susceptible to cracking for reasons described earlier. Nonetheless, these vessels which have never been acid cleaned are (statistically) less susceptible than stress-relieved vessels that have been acid cleaned. On the other hand, a European mill that has never been acid cleaned showed severe and repeated cracking after a short period of operation. Similarly, impregnation vessels in two-vessel systems have no extraction screens requiring acid cleaning, yet cracking has been severe in these impregnation vessels. At best, the evidence regarding cracking in vessels that have not been acid cleaned is contradictory.

Thus, it appears that acid cleaning is not a controlling variable in the onset of digester cracking. For reasons discussed in the section on sulfide cracking, this insensitivity to acid cleaning is not unexpected.

#### Wood Species

Since the species of wood pulped in digesters is known to affect the corrosion characteristics of digester vessels (60), SCC susceptibility might also be affected by the wood species pulped. Many of the responses to the updated TAPPI survey included information on the type of wood being pulped in each digester. This information is summarized in Tables VI and VII. As seen in Table VI, there may be a correlation between cracking susceptibility and operation with mixed hardwoods and softwoods. Softwood, hardwood, and alternating HWD/SWD operation does not apparently influence cracking susceptibility. In Table VII, the actual wood species pulped at each mill are tabulated for each vessel for which a response is available, and in Table VIII, the tallies are summarized. The vessels showing immunity pulp a variety of woods, but the vessels showing severe, type A cracking are somewhat more likely to pulp southern pine and southern hardwoods. The evidence does not implicate one or more species as being responsible for digester vessel cracking.

TABLE VI

#### CORRELATION OF WOOD TYPE AND CRACKING SUSCEPTIBILITY

Wood Type	Grade A	Grade B	Grade C	Grade D
Softwood	13	6	6	16
Hardwood	3	2	1	4
Alternating HWD/SWD	4	-	1	4
Mixed HWD/SWD	12	3	-	4

---

\*A is severe cracking, D is no cracking.

TABLE VII  
CORRELATION OF WOOD SPECIES AND CRACKING SUSCEPTIBILITY

Grade A Cracking		Grade B Cracking		Grade C Cracking		Grade D Cracking	
Mill	Species	Mill	Species	Mill	Species	Mill	Species
002	14	005	15	006	22,7,28	001	24
011	14,24	016	24	052	22,7	009	5,19,8
014	19,23	031	24	069	18,21,19,29	015	23
022	5,9	041	28,13,24	078	22,28,7	018	18,19
024	19,5	042	14,24	109	25,16,26,27	029	5,19,21
039	14,24	074	14	141	22	036	5,3,28
043	24	086	16,26	147	15	038	14,24
048	14,24	088	24			056	22,5,7,1
058	14,24	090	24,14			057	29,26,30,9
063	25,16,27,24	129	27,16,15			060	14,24
071	19,5,2	134	14			061	25,26,26,27
075	10,9,7,28	148	14			065	5,19,21
076	14					080	7,22,21,5
079	15,16					091	5,28
085	14,25,26					093	1
087	14,24					097	9,16,29,26
102	14,24					098	14,1,4,7
105	15,27,16					101	24,1,14
112	14,24					108	22,5,1,7
114	14					110	15,19
118	10,9,1,2,5					113	24
122	15,24					115	19,5
127	5,3,8					121	2,28,10,5,4
128	23					133	5,28,22
131	10,28,22					145	14
143	19,5					146	5,21,23
144	19,5,22,28,7						
149	5,3,28						
150	5,3,1,21						

Code

1 Douglas-fir	7 Western Red Cedar	13 Redwood	19 Jack Pine	25 Sweet Gum
2 Western Larch	8 Balsam	14 Southern Pine	20 Red Spruce	26 Maple
3 Lodgepole Pine	9 White Pine	15 Loblolly Pine	21 Balsam Fir	27 Hickory
4 White Fir	10 Ponderosa Pine	16 Oak	22 Hemlock	28 Fir
5 Spruce	11 Alder	17 Alpine Fir	23 Northeast Hardwoods	29 Poplar
6 Western Hemlock	12 Cottonwood	18 Black Spruce	24 Southern Hardwoods	30 Birch

TABLE VIII  
CRACK CODE RESPONSES

	Species	A	<u>Cracking Severity*</u>		D
			B	C	
1	Douglas-fir	2			5
2	Western Larch	3			1
3	Lodgepole Pine	4			2
4	White Fir				2
5	Spruce	9			11
6	Western Hemlock				
7	Western Red Cedar	2		2	4
8	Balsam	1			1
9	White Pine	3			2
10	Ponderosa Pine	3			1
11	Alder				
12	Cottonwood				
13	Redwood		1		
14	Southern Pine	11	5		5
15	Loblolly Pine	3	2	1	1
16	Oak	3	2	1	2
17	Alpine Fir				
18	Black Spruce			1	1
19	Jack Pine	5		1	6
20	Red Spruce				
21	Balsam Fir	1		1	4
22	Hemlock	2		4	6
23	Northeast Hardwoods	1			1
24	Southern Hardwoods	10			6
25	Sweet Gum	2		1	1
26	Maple	1	1	1	3
27	Hickory	3	1	2	1
28	Fir	4	1	2	4
29	Poplar			1	2
30	Birch				1

\*A is severe cracking, D is no cracking.

### Chip Versus Sawdust Digesters

Since sawdust digesters are usually smaller than chip digesters, it is to be expected that the sawdust digesters would be somewhat less susceptible to cracking. However, it also seems likely that the sawdust vessels have not received the NDE attention focused on larger chip digesters, and so mills would be less likely to find cracks in the sawdust digesters. Indeed, less cracking susceptibility is seen. Of the eight sawdust vessels for which information is available, all but one are in the Grade C and Grade D categories; one vessel has exhibited Grade B sources; but none have demonstrated severe Grade A cracking.

### Vapor Phase/Two Vessel Systems

Both steam phase digester systems and two-vessel systems reflect the general cracking tendencies of the hydraulic digesters. This is not surprising for two-vessel systems but may be surprising in the case of vapor phase digesters. In these steam phase vessels, the nominal impregnation zone is not immersed in a chip/liquor slurry, but is instead exposed to injected steam and any volatile species evolved from the chip mass. Even though the top of the vessel is not immersed, at least one vapor phase vessel has exhibited cracking in the steam phase region, with deep cracking in a vertical weld. Apparently, the species responsible for cracking can be deposited on the vessel walls and form a liquid layer capable of causing cracking.

### White Liquor Characteristics Versus Cracking\*

Many of the mills responding to the updated questionnaire provided information regarding their white liquor characteristics. As is usually the case, this information was provided in a variety of formats and terminologies, but the data have been condensed into three representative quantities: active alkali expressed as  $\text{Na}_2\text{O}$  g/L, total titratable alkali expressed as  $\text{Na}_2\text{O}$  g/L, and percent sulfidity on an AA basis. Active alkali (AA) includes the  $\text{NaOH}$  and  $\text{Na}_2\text{S}$  present in the white liquor, converted into equivalent grams per liter of an imaginary  $\text{Na}_2\text{O}$  compound. Total titratable alkali includes the AA plus the  $\text{Na}_2\text{CO}_3$  content of the liquor, expressed in grams per liter of equivalent  $\text{Na}_2\text{O}$ . Sulfidity is the ratio of  $\text{Na}_2\text{S}$  to active alkali, with all quantities expressed as  $\text{Na}_2\text{O}$  in the calculation\*\*.

White liquor conditions are quite uniform from mill to mill. As shown in Table IX, the AA values ranged from 69 to 119 g/L as  $\text{Na}_2\text{O}$ , but most active alkali figures are in the 85-110 g/L range. Typically, the TTA values are higher by about 10-15 g/L as  $\text{Na}_2\text{O}$ . Sulfidities vary from 21 to 42%, with most in the 25-35% range. One Kamyr digester pulps without  $\text{Na}_2\text{S}$  using the soda process, rather than the kraft process. The white liquor properties reported in Table IX are similar to those previously reported for continuous digester operation (61,62).

---

\* Additional information on white liquor correlations versus liquor characteristics is presented in the detailed account of liquor sampling at six selected mills.

\*\* Sulfidities may also be expressed on a TTA basis, in which case the denominator in the sulfidity expression is the TTA (as  $\text{Na}_2\text{O}$ ). All sulfidities are taken as AA basis sulfidities where the intent of the survey response is unclear. The error in the sulfidity number is certainly less (~ 10%) than the routine changes in sulfidity at a typical mill.

There is no significant correlation between the average white liquor properties and propensity toward cracking in continuous digesters. As shown in Fig. 34, the combinations of sulfidity and active alkali span the same range for seriously cracked vessels and for immune vessels. Removing data for stress relieved vessels and considering only non-stress-relieved vessels does not alter this pattern, as shown in Fig. 35. Considering sulfide concentration, rather than sulfidity as in Fig. 34-35, will not affect the basic message of these figures since the liquor data for cracked and uncracked mills will continue to show the broad similarities shown in these figures. Comparisons with total titratable alkali only have the effect of shifting the scale on the abscissa to concentrations 10-20 grams per liter higher than those shown in Fig. 34 and 35. Similarly, causticizing efficiency does not correlate with the susceptibility to SCC in vessels. Based on these results, it is clearly evident that the general white liquor characteristics used with any vessel do not control digester vessel cracking susceptibility.

A further attempt to relate cracking susceptibility to general mill operations was made by consulting published summaries of pulp mill information (63) -- products, equipment, water use, etc. -- and comparing these variables for immune and susceptible mills. No justification is made for the attempted correlations, other than the reminder that recovery, recausticizing, and papermaking practices can often change the liquor conditions in the kraft mill.

The following mill variables were examined for possible correlation with cracking susceptibility.

- (1) Production of bleached and unbleached hardwood or softwood pulp
- (2) Final mill product
- (3) Black liquor oxidation practices
- (4) Black liquor evaporator stages



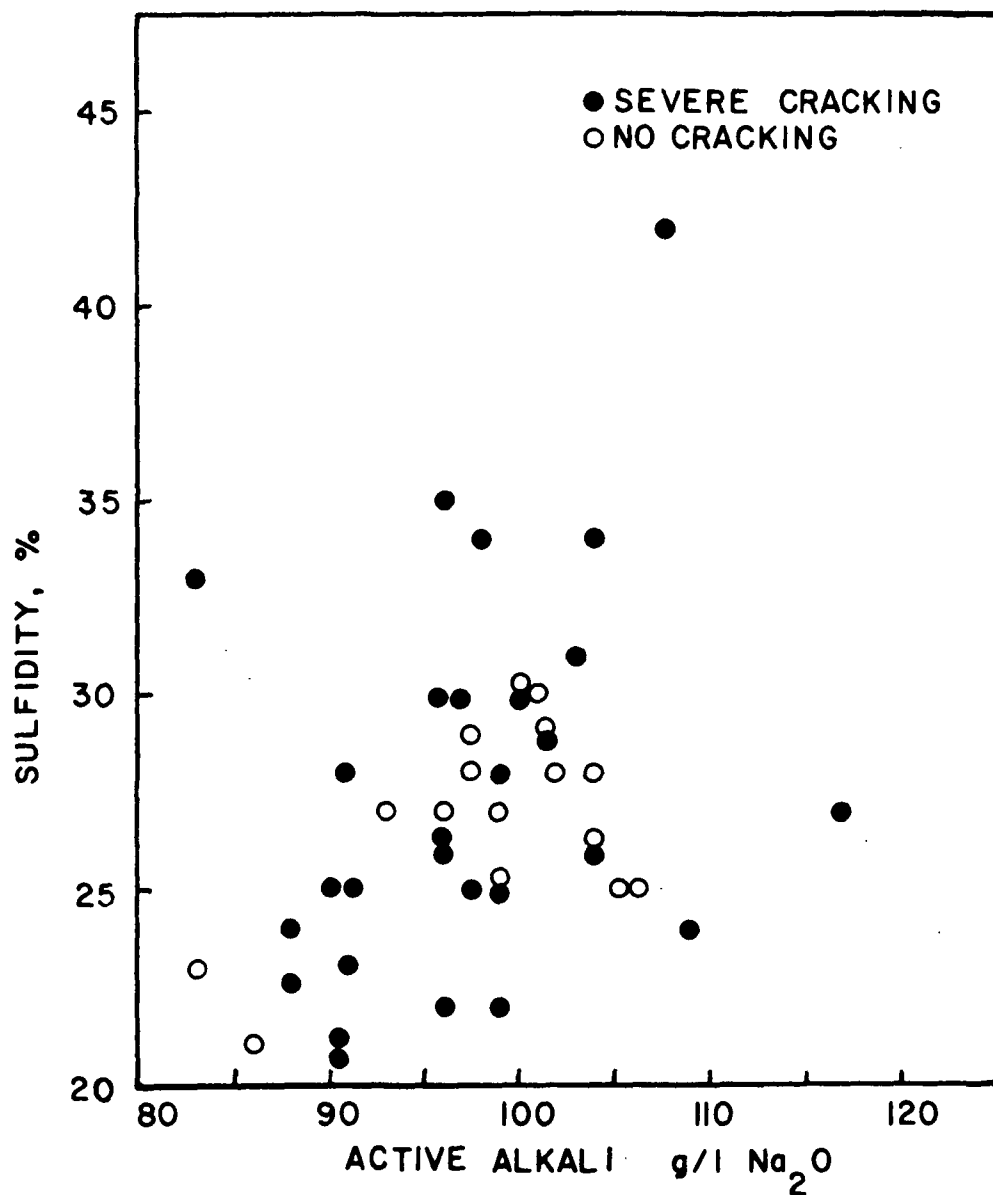


Figure 34. Cracking susceptibility versus white liquor properties.

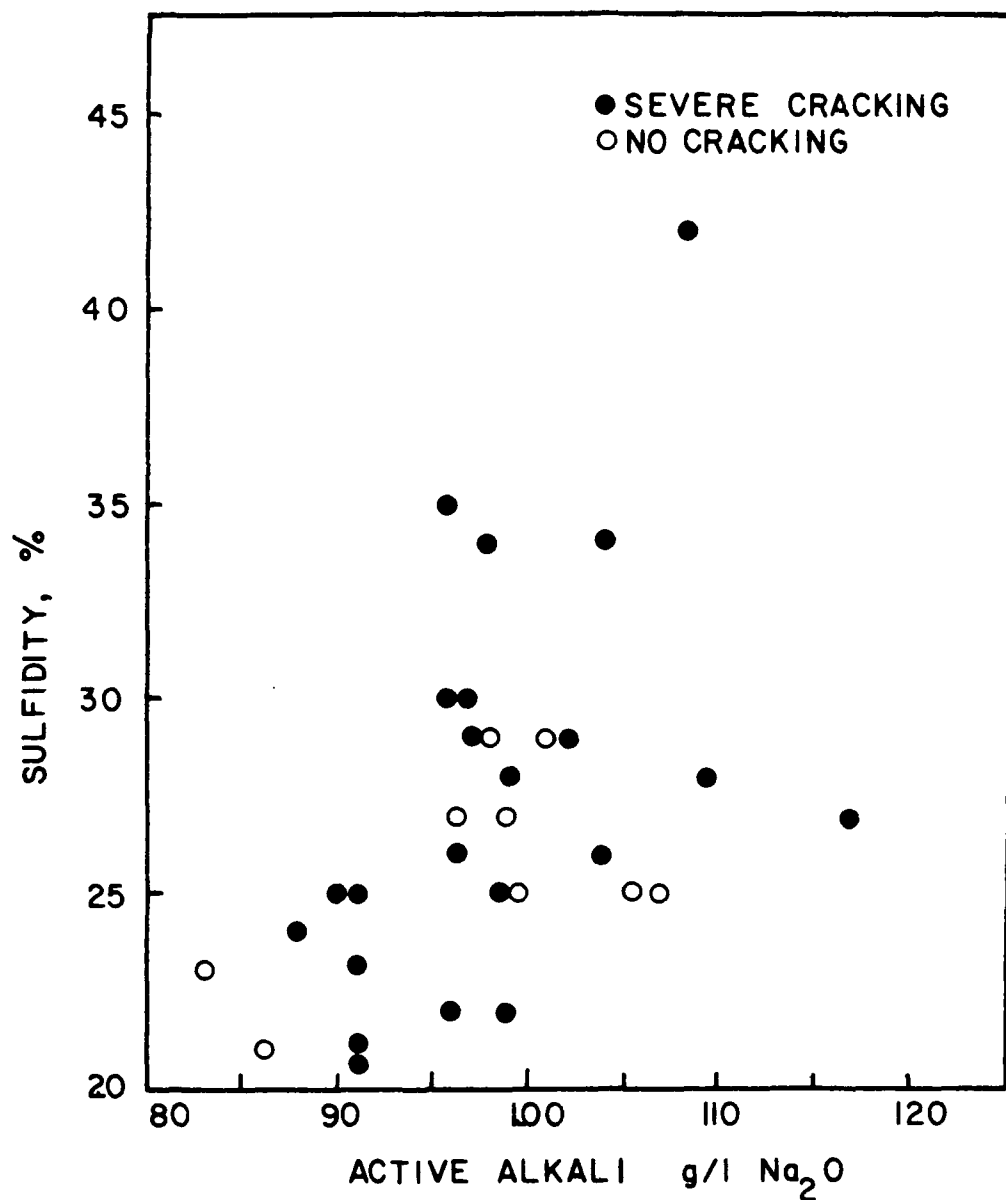


Figure 35. Cracking susceptibility versus white liquor properties for non-stress-relieved vessels.

TABLE IX  
CORRELATION OF WHITE LIQUOR CONDITIONS AND CRACKING\*

Grade A Cracking			Grade B Cracking			Grade C Cracking			Grade D - No Cracking		
Mill	AA	TTA	Mill	AA	TTA	Mill	AA	TTA	Mill	AA	TTA
-002	90.8	107.8	005	96.5	113.5	006	101.7	115.9	-001	82.8	100.3
-011	107.7	127.6	016	82.8	100.4	010	68.9	115.1	-009	99.2	116.8
-012	104.0		041	96.0		052	100.5	112.0	-018	102.0	
-022	96.0		086	92.8	99.2	069	96.0		029		
-024	88.0	104.0	090	101.6	126.0	078	98.6		036	100.0	
030	109.0	132.0	129	119.2		109	97.6	123.9	-038		
-039	90.6	120.1	134	87.6	109.1	141	101.7	115.9	056		124.8
-043			148		121.0	147	96.5	113.5	057		
-048	90.6	120.1							-060	105.6	125.2
-058	99.1	123.7							-061	97.6	123.9
-063	104.0	124.8							-065		
-071	99.2								080	100.0	
075	96.0	115.2							091	104.0	
-076	96.0	115.2							093	97.6	113.6
-085	97.6	123.9							097		128.0
-087	96.5								-098	107.2	123.2
-102	90.8	113.5							-101	101.6	126.0
112	103.0	118.0							108		124.8
-114	101.6	126.0							-110	86.0	103.0
-118	99.2	112.0							-113	99.1	123.7
-122	90.2								115	92.8	110.4
-127	83.2	112							-121	96.0	118.4
-131	90.8								-124		124.8
-137	117.0	128.5							-133		124.8
-143	97.8	112.0								104.0	
-144	96.0										
149	100.0										
-150	96.0	112.0									

\*AA and TTA as g/l. Na<sub>2</sub>O.

- (5) Reausticizing system design
- (6) Recovery boiler type
- (7) Bleaching practices, sequence
- (8) Water usage
- (9) Water source

None of these variables affected cracking susceptibility of the continuous digester vessels. For example, the digesters at mills with bleach plants are no more susceptible to cracking than those without bleaching capabilities, even though some of the by-products of bleaching chemical generation are usually disposed of in the recovery process stream. Twenty-eight of forty-one mills reporting severe, Grade A cracking in their digesters also operate bleach plants; for Grade D immunity, the fraction of mills operating bleach plants is 12 out of 39. There is also no apparent correlation between cracking and bleach plant sequence. Fine paper mills are as susceptible as kraft linerboard mills. Black liquor oxidation does not correlate with cracking susceptibility, nor does the recausticizing system design. Cracking occurs with equal frequency at mills with Combustion Engineering (CE) and Babcock and Wilcox (B & W) recovery boilers. Cracking is equally likely for mills using river water, lake water, or well water. None of these variables was found to affect overall susceptibility to digester cracking.

#### Detailed Questionnaire Results at Six Selected Mills

The six mills selected for on-site liquor chemistry measurements were also asked to fill out the detailed questionnaire found in the Appendix. The questionnaire had three sections dealing with digester operation, recovery practices, and recausticizing practices. Because of the detail involved, less than total success was achieved in obtaining fully completed questionnaires from all mills. In many cases, the information requested was simply not available because

measurements have not been made. However, responses were obtained from both immune and susceptible mills for possible correlation with their susceptibility.

The recovery and recausticizing practices at all of the mills responding were similar.

With the exception of minor changes in liquor chemistry and wood species used at each mill, the details of the recovery procedure were not different from mill to mill. Water added to the recausticizing process stream came from the same source. Temperatures and concentrations at each of the stages in the recausticizing process varied by only a few percent from mill to mill, and no trend was apparent for correlation with cracking susceptibility. Few additives were used in the recausticizing process stream. One of the mills whose digester had Grade A cracking used a small amount of corn starch to promote settling of suspended solids; another mill added Nalco polymer at the lime mud washer and dregs washer. One mill added spent acid from the bleach generator to the white liquor clarifier, but no other process streams were mixed with the recausticizing liquors in any of the mills.

The recovery processes used at the immune and susceptible mills responding to the questionnaire were also very similar. Every mill used a defoaming agent in the pulp washing stages, although a different agent was used at each of the mills and no correlation was possible. There was no correlation of cracking with diffusion and drum washing practices. The liquor evaporation processes were also virtually identical at each of the mills. One mill did not practice black liquor oxidation, and that mill had a digester with severe cracking. The rest of the responding mills oxidized strong black liquor to a very low residual sulfide level. Kerosene was added to suppress foaming at one

mill with an immune digester. All of the mills employed multiple effect, long-tube-vertical evaporation, and all experienced some moderate problems with scale buildup in the first effects every four to twelve months. The concentration of solids into the recovery boiler was virtually the same from mill to mill (close to 70%). Half of the mills did not operate tall oil recovery plants, but there was no correlation with cracking susceptibility. B & W and CE recovery boilers were in use at the mills, but the boiler type did not correlate with cracking susceptibility. A variety of precipitators was in use, but nothing associated with precipitator operation or design could be related to cracking susceptibility. Nothing but concentrated black liquor and occasional fuel (oil or natural gas) was burned in the recovery boilers surveyed. Only one of the four mills -- a mill with severe digester cracking -- added salt-cake makeup at the recovery boiler; the salt cake came from tall oil recovery or was purchased. All of the mills claimed a high degree of reduction efficiency of 90% or higher. Only one of the mills was able to provide a detailed analysis of black liquor composition, so no relationship between black liquor and cracking conditions was possible. Combustion conditions were also the same at all of the mills. Thus, because of a high degree of similarity of recovery processes at the mills visited, no correlations with cracking susceptibility could be identified -- immune and susceptible mills were virtually the same.

Similarly, most of the routine digester operations were similar at the different mills, so no correlation between cracking and digester operations was possible. An exception was a two-vessel, steam phase digester that had exhibited severe cracking -- the operation of this vessel was naturally somewhat different from that used at hydraulic vessels. The method of chip level sensing was not a significant variable in cracking, since most mills employ top separator screw torque sensors or paddle sensors to detect complete filling of their

vessels. The top circulation temperatures ranged from 220°F to 240°F. The retention time for chips in the impregnation zone (or vessel) ranged from 30 to 55 minutes, again without a significant correlation with cracking behavior. All of the mills admitted some black liquor to the cooking liquor at a few gallons per minute, usually only during upset conditions. One of the mills (a mill with severe cracking) added black liquor in the summer only at a rate equal to one-fifth of the white liquor flow rate to the vessel. Impregnation zone temperatures of 230-240°F were reported; upper and lower cooking temperatures were in the range 280-310°F and 340-365°F, respectively. (In the vapor phase digester, of course, cooking occurs by direct admission of live steam at the top of the vessel).

In all cases but one, routine acid cleaning using inhibited hydrochloric acid was practiced by all of the mills; formic acid was used in the exceptional case. No correlation with cracking was evident in acid cleaning practices, as expected from arguments presented earlier.

Batch cook start-up practices follow the Kamyr recommendations, so there is little variation from mill to mill, and none that correlate with cracking susceptibility. One mill without a high susceptibility to cracking fills the digester with black liquor before adding chips or cooking liquor. In every case, the vessel is completely filled with chips before beginning the batch cook, so the impregnation zone does not appear to be bathed in raw white liquor without the moderating influence of chips during this time.

In general, vessels are acid cleaned and air dried during any prolonged shutdown period. Therefore, cracking is probably unrelated to lay-up procedures during shutdown.

The detailed responses to the questionnaire augment the observations made from the general TAPPI Task Group survey questionnaire -- kraft mills are similar in operation and design, and those minor differences that separate the individual mills cannot be unequivocally related to digester operation.



### SUMMARY

Based on the preceding sections, it is clear that cracking is not restricted to some vessels operated beyond the limits of some acceptable pulping chemistry. Furthermore, it is clear that the macroscopic variables associated with pressure vessel construction, such as welding procedure and base metal selection, do not control digester cracking susceptibility, with the exception of benefits accrued from stress relief. It is comforting to learn that operation within the normal bounds of kraft pulping will not expose a vessel to unusual jeopardy from stress corrosion cracking. It is equally frustrating to learn that cracking in continuous digester vessels cannot be suppressed by changing pulping operations to conform with those in use at mills where vessels have been immune.

## REMEDIES FOR VESSEL CRACKING

### INTRODUCTION

The objective of this section is to provide a brief account of the interim measures taken to remedy SCC in continuous digester vessels and, where possible, to summarize the record of success or failure of each measure. Many mills have resorted to untested measures in an attempt to repair the damage caused by stress corrosion cracking and, occasionally, to prevent its future recurrence. In some cases, repeated inspections have demonstrated the success or failure of these remedial measures. Some of the information gathered in this repair/reinspection process has been shared with the TAPPI/IPC Program on Digester Cracking and is summarized below.

A cautionary note must be expressed concerning the nature and accuracy of this section. This section is based on the voluntary responses of a fraction of the mills that have employed remedial measures, so the survey is necessarily incomplete. Reports of success or failure of a given remedial measure based on such a small sampling may not give a true picture of the effectiveness of that measure. Descriptions and accounts of repair method effectiveness cited here may be influenced by the individual biases of the reporters. In some cases, the success or failure of a remedial measure may be very sensitive to the skill and experience of the operator making the repair, or on the willingness of the mill to pay for (and wait for) a proper repair. In such cases, a poor execution of an acceptable repair measure can taint what otherwise might be an attractive remedy. Conversely, a successful implementation of a repair at one mill does not ensure the same degree of success at another mill. Finally, the repair of digester damage and attempts to prevent future occurrences is a new venture. In

some cases, mills have learned from early mistakes that should not continue to haunt a remedial measure that has been improved.

A number of repair/preventative measures have been used in continuous digester vessels, ranging from simple grinding to complete overlaying of a vessel. Each of the following sections deals with the details of the repair/prevention measure, and the current assessment of its success.

#### REPAIR BY GRINDING

It appears that some relief from recurrent cracking is obtained when welds with shallow cracks are ground to remove the cracks or to prepare the surface for WFMT inspection. In several cases, reinspection 6 months after grinding revealed no new indications in the ground areas, although cracking was detected in adjacent, previously unground areas. However, it is likely that the cracks in previously unground surfaces were also present at the time when the first grinding was done. In at least one case, ground welds did not exhibit recurrence of cracking in the affected welds after a 12-month exposure to cooking liquors.

Unfortunately, there is also abundant evidence that surface grinding alone is generally inadequate to prevent the recurrence of cracking at digester weldments. This is particularly true for the recurrence of short longitudinal and transverse cracks appearing in the weld cap region.

#### REPAIR BY WELDING

When cracks penetrate the vessel to a depth exceeding the 1/4" corrosion allowance, there is little option but to grind out the cracked areas and reweld with an appropriate procedure. In virtually every case, welding has been

performed manually using low hydrogen E7018 electrodes and some preheat. The typical preheat ranges from 200°F to 400°F, with the 200°F preheat recommended by the ASME code for original construction only for walls exceeding 1 1/4" in thickness. The universal practice is to complete enough passes to restore the original wall thickness. In two instances, the repaired welds were given a complete postweld heat treatment (~ 1000-1100°F for 2 hours). In another vessel, the repair welds were applied using the temper-bead welding technique, with more than 75 weld passes used to complete a weld buildup of one-half inch. (In temper bead welding, a portion of the weld bead from the previous pass is removed before the next pass is made, to ensure that the heat supplied by the current pass "tempers" or stress relieves the previous weld). Another mill has used a low silicon electrode in its weld repair program.

The large number of vessels which have re-cracked after repair welding is distressing. Repaired fillet welds attaching the downcomer support to the shell have shown through-wall cracking at the repair in eighteen months. In several other vessels, repeated re-cracking of repair welds has led mills to a routine of overlaying repaired welds with a stainless alloy. The morphology of cracking in weld repairs is similar to that reported for the original welds, with the most serious cracking occurring in the HAZ of repair weldments. In many cases, the re-cracking is less severe than the original cracking, but the exposure times are also much shorter than for the original welds.

The postweld stress relief treatments were only marginally successful in suppressing re-cracking of repaired welds. At one mill, repaired-and-stress-relieved welds had exhibited cracking within six months, with additional cracking in the next six-month period. At another mill, the heat-treated weld

repairs exhibited cracking less than 1/8" deep after a 14-month exposure to digester conditions.

For unknown reasons, some weld repairs made in digesters have not exhibited any evidence of re cracking. Several mills reported that weld repairs made early in the life of a vessel to remedy localized corrosion problems are intact and without cracking after many years of service. Preheat temperatures in the range of 70°F to 400°F had no mitigating effect on re cracking. In one vessel, a weld repaired with 450°F preheat did not crack. Weld repairs have survived 12-month exposures without cracking in a number of vessels that had previously exhibited deep cracks.

Welded repairs in the stress relieved zone of a vessel can apparently induce cracking where none was previously encountered. In two stress relieved vessels with long service without cracking, weld repairs made to correct a localized corrosion problem were cracked within six to fifteen months -- the only cracks evident in the vessel.

The effect of the temper bead welding procedure on re cracking susceptibility is unknown at present, since reinspection of the repaired area is not scheduled for 12 months. The effect of low Si weld repairs is also uncertain due to the lack of reinspection data.

Thus, the record of re cracking in weld repaired areas is scattered. Some repair welds endure without re cracking, and some crack so quickly that shell penetration occurs within a year. Obvious differences in welding procedures that correlate with re cracking are not evident, although the documentation of repair welding procedures is usually scanty. There is, at present, no

alternative to repair welding when cracking or localized corrosion penetrates the corrosion allowance. Frequent recracking of repaired welds has provoked considerable attention to alternative measures to prevent recracking, as described below.

#### CRACK PREVENTION BY SHOT PEENING

At present, at least 12 vessels have resorted to shot peening of original or repair welds in an attempt to suppress stress corrosion cracking by inducing compressive residual stress patterns in the surface of the weldment. The usual practice has been to grind the welds as completely as possible to remove pits and other surface irregularities before peening with steel shot in the 170 to 250 size range. In the early peening efforts, little attention was directed toward questions of coverage and intensity. As evidence of recracking at peened areas become available, greater care was taken to insure complete coverage (150% is typical) at a controlled intensity, using coverage-indicating coatings and Almen gage strips, respectively. The peening process is relatively fast and economical.

There is little doubt that a one-time shot peening application is insufficient to suppress cracking in weldments. After a single peening operation, most of the mills reporting reinspection data found that their vessels had some evidence of recracking. At one mill where shot peening was carefully examined, cracking had recurred in peened welds six months after peening, although the severity of cracking appeared to be reduced on peened areas. A similar experience was reported at a second mill, where areas of recracking after 6 months were ground slightly and repeened. In this latter vessel, recracking was associated with pits that had not been completely removed prior to peening.

After a second six-month exposure, the evidence of re cracking was reduced still more, approaching acceptable levels of recurrence. The peening, exposure, examination, and repeening process may be effective in discovering areas where inadequate peening took place in earlier repairs, so that repeening can be done to those areas. It is clear that this repeening process is much more effective than a single peening application. Several mills have adopted this repetitive peening procedure.

There have been no reports of any systematic examination of the principal peening variables -- shot size and type, intensity, coverage, etc. -- on the efficiency of peening as a remedy for cracking. In a single investigation, there was no significant effect of shot size in the range 230 to 250. It is possible, therefore, that the peening conditions currently being used are not optimized for increased cracking resistance. The long-term endurance of shot peening as an effective remedy is also uncertain because of the shallow depth of the compressive layer and the unknown role of corrosion in eliminating the protective layer.

#### CRACK PREVENTION BY STAINLESS ALLOY OVERLAYS

There is little doubt that stainless weld overlays endure in the continuous digester environment. A TAPPI Task Group has chronicled the performance of weld overlays in continuous digesters for a number of years and concluded that their performance in continuous digesters was far better than in batch digesters where continual maintenance is required (64,65).

The record of performance of stainless overlays has also been good in recent years as a remedial measure to alleviate cracking. In several cases, stainless overlays have been the measure of last resort because of repeated

cracking associated with weld repairs and other remedial measures. In every case, the placement of stainless steel, Inconel, or similar overlays has prevented continued degeneration of digester weldments.

Most of the overlays placed over digester welds have been Inconel 82 material placed with automatic MIG techniques. In some cases, 308 and 309 stainless steels, Inconel 182 (SMAW), Eutectic 2222XHD, and Incoweld A have also been used with success. Difficulty in manual placement of Inconel 182 material was reported to have been resolved by placing a 7018 overlay on the weld before attempting the Inconel weld. The use of pulsed-arc MIG techniques in placement of Inconel 82 weld overlays has eliminated most of the difficulties associated with manual overlays with Inconel 182.

There has been concern about the HAZ adjacent to the outermost passes of the overlay and the effect of these zones on crack initiation and growth in the substrate metal. In one case, this concern was obviated by a complete overlaying of the interior of the vessel -- an impregnation vessel in this case. Examination of the HAZ region adjacent to overlays after 6-month and 12-month exposures to cooking liquors has revealed some very shallow cracking in the zone of both Inconel and stainless steel overlays. There has been no evidence of continued penetration of this mode of cracking. As might be predicted from the results of the Cavanan surveys (64,65), dye penetrant tests have shown no evidence of cracking in stainless overlays themselves. The irregular surface of the overlay makes high resolution examination difficult, but it seems clear that no serious defects have occurred in the stainless overlay material. The longest known exposure of a stainless alloy as a remedy for cracking is now approaching 4 1/2 years. Of course, the Cavanan study (64,65) documents much longer exposure.



Although no mill has reported attempts to use stainless liners welded to the inside of digester vessels, the experience with stainless-clad top heads indicates that the welds holding the plates in place may be susceptible to attack. Many mills have encountered stress corrosion cracking of the stainless cladding in the heat-affected zones of welds in the top head area. Welded stainless liners in the impregnation zone may suffer a similar fate.

#### CRACK PREVENTION BY THERMAL SPRAY COATINGS

The experience with plasma sprayed metal coatings as barriers preventing liquor contact with welds has been restricted to one mill site. Three plasma sprayed metal coatings -- Metco 444, Alloy 2148, and Hastelloy C -- were applied to welds in a severely cracked vessel. In some cases, the metal coatings were sprayed over welds that had first been shot peened. Careful surface preparation was used in each case.

The coatings were intact after a 6-month exposure in the digester vessel, but had separated from the carbon steel wall after a total exposure of 14 months. There was little evidence of attack in the metal coatings themselves, but all three coatings had debonded from the vessel wall in large patches. The decohesion was similar for peened and unpeened substrates.

Based on speculation that the coating had come loose because of corrosion that initiated at pores in the coating, the Metco 444 plasma sprayed coating was replaced and sealed with a silicone sealant. The sealant was selected to seal the pores in the plasma sprayed coating, thereby preventing the initiation of corrosion that leads to coating delamination. After a 6-month exposure, the sealed coating was inspected and found to be intact. The silicone sealer was again sprayed on the plasma sprayed surface, and the vessel was

returned to service. The next inspection will reveal whether the durability of the sealed coating will exceed the six-month durability of the unsealed Metco 444 coating.

#### THERMAL STRESS RELIEF IN SITU

In three cases, repaired vessels were stress relieved in situ in the impregnation zone area in an attempt to reduce residual stresses associated with the weldments. In one case, there had been extensive refabrication of the impregnation zone, and the stress relief was similar to heat treatment of a new vessel. However, in the other cases, the vessels were stress relieved at each of several girth welds in the impregnation zone after the vessel had cracked in service. A technique was developed to stress relieve individual welds without removing the internal and external attachments to the vessel. No problems were encountered in this in situ annealing.

In the refurbished vessel and one of the other stress relieved vessels, there was extensive cracking of the stress-relieved welds after 6 months of operation.

In the case of the third vessel, reinspection after a year of operation revealed only a very shallow cracking in the welds that were stress relieved in situ. The shallow cracking was no worse at the site of an extensive repair made before stress relieving was done.

#### ANODIC PROTECTION

Anodic protection is theoretically possible in digesters if the laboratory results indicating a narrower range of potentials for SCC in alkaline sulfide media are relevant to actual digester conditions. The practical

implementation of an anodic protection system for preventing cracking in digesters requires durable hardware and evidence of sustained maintenance of a potential outside of the cracking potential range.

At present, there are four anodic protection systems in various stages of operation in the United States. The oldest of these was installed in 1979 in a soda digester to reduce excessive localized corrosion. In 1981, an inspection of the vessel for cracking revealed shallow cracking in several welds in the impregnation zone. It was unknown whether or not these cracks occurred in the 9 years before the anodic protection system was in place. Some of the cracks were removed by grinding at this inspection. In a subsequent inspection one year later, there was no evidence of cracking in the areas of the weld that were ground the previous year. Based on this limited evidence, one might conclude that anodic protection has suppressed cracking in a soda digester. However, the evidence is far from unequivocal, and more concrete evidence of protection will be sought in future years.

The operation of two of three anodic protection systems on kraft digesters has not been trouble-free. Some problems have been encountered in the hardware used in the protection system -- problems not unexpected as a new technology is readied for commercial usage. However, because of the interruptions, there can be no interpretation of the effectiveness of anodic protection as a control measure for kraft digester cracking. The third anodic protection system for kraft digesters was brought on line in the Fall of 1982.

## CHEMISTRY AND ELECTROCHEMISTRY OF KRAFT LIQUORS AT SELECTED MILLS

### INTRODUCTION

At the start of this program, very little was known about the actual chemical and electrochemical conditions that existed in the impregnation zone of continuous digesters. To be sure, the incoming white liquor characteristics were known and controlled, but the chemistry of the liquor after it had been recirculated while in contact with wood chips was not known. The rate of consumption of cooking chemicals during the low-temperature cooking that occurred in the impregnation zone was also unknown. Finally, there was virtually no published information regarding the electrochemical behavior of carbon steel in these environments.

This primitive level of understanding presented three problems affecting the resolution of the digester cracking situation. On one hand, the uncertainty regarding the actual environments present at the site of cracking prevented an understanding of the role of cooking liquor variables on stress corrosion cracking propensity. If the role of these liquor variables is not clear, the modification of liquor chemistry to attempt to control cracking can only be done by trial and error. On the other hand, the poor understanding of actual liquor chemistry at the sight of cracking confounds the choice of an appropriate test medium for use in laboratory tests that will be used to check the effectiveness of candidate remedies. Finally, the inadequate understanding of the electrochemistry has confused the degree of protection required for successful use of anodic protection measures.

The Institute of Paper Chemistry proposed an intensive study of the chemistry and electrochemistry of the kraft cooking liquors with an early

completion date so that the results would be useful to the DCRC steering committee and its research contractors. A turn-around time of four months was anticipated. The study involved visits to six mills -- three with severe cracking susceptibility and three with no susceptibility -- to characterize the cooking liquors and determine if some characteristic of the liquors could be correlated with cracking susceptibility. At the same time, liquors were to be analyzed to determine the chemical composition of accessible liquors, in an attempt to define liquor conditions inside the impregnation zone of the digester vessel. A third aspect of the site visit, the gathering of detailed operating information, has already been described in Section V. The DCRC accepted the Institute's prepared work plan; this section describes the approach used in the subsequent study and the results of the chemical and electrochemical studies of liquor characteristics.

## EXPERIMENTAL APPROACH

### Objective

The objectives of the mill visits were to analyze the chemical composition of liquors relevant to continuous digester operation and to determine the electrochemical behavior of carbon steel exposed to these liquors. These objectives were accomplished by using an apparatus that continuously passed extracted liquor samples through a series of chambers where the temperature conditions spanned the range of interest in the digester, and where electrochemical measurements could be made in situ on liquors in the apparatus. In addition, provisions were made for occasional grab sampling of liquors for chemical analysis, or for isolating grab samples of liquors that caused any change in the redox potential of the liquor. Using this apparatus, the chemical characteristics of cooking liquors were determined for each of the six mills visited,

together with an electrochemical characterization of a carbon steel and a weld metal in these liquors.

### Mill Site Selection

Six mills were selected for study, based on cracking susceptibility, geographical location, diversity of kraft processes used, and willingness to cooperate in the program. Since the effect of stress relief was already apparent, none of the digesters selected for study were stress relieved in the impregnation zone. Characteristics of the selected mills included:

- Small and large digesters
- Older and newer digesters
- Southern, Midwestern, Eastern, and Canadian mills
- A vapor phase digester and hydraulic digesters
- A two-vessel digester and one-vessel digesters
- Digesters with all of the common welds and base metals
- Digesters with a range of cooking liquor chemistries
- Digesters involved in the manufacture of a variety of final products

To preserve the confidentiality of the information obtained at the mills, the mills were coded as follows:

- Mill 60 - a relatively new hydraulic digester of medium size without significant cracking; alternate SWD/HWD pulping
- Mill 62 - a small hydraulic digester without significant cracking; alternating HWD/SWD pulping
- Mill 110 - an older hydraulic digester without significant cracking; pulping SWD
- Mill 137 - a smaller, older hydraulic digester; alternate HWD/SWD pulping with serious cracking

- Mill 143 - a large two-vessel, steam-phase digester pulping SWD,  
with serious cracking
- Mill 48 - a newer, large hydraulic vessel pulping mixed SWD/HWD,  
with serious cracking.

All of the uncracked vessels had been inspected with magnetic particle methods and had been found free of cracks. All of the cracked vessels had cracking serious enough to warrant repairs. The Pine Hill vessel was specifically excluded from consideration.

All of the mills contacted expressed considerable reluctance and, in several cases, outright refusal, to grant permission to tap into the high pressure portions of the vessel during operation, because of safety concerns and concerns about accidental loss of vessel production. Thus, it was not possible to sample liquors directly from the top circulation line or the impregnation zone, although mill 143 with the two-vessel system did provide a grab sample from the high-pressure line connecting the impregnation vessel to the digester vessel. In another case, top recirculation liquor was obtained at a leaking valve at Mill 60, but some slight flashing of this sample caused it to be slightly concentrated. The Institute proposal provided for sampling of cooking liquors at the low-pressure side of a feed pump, and then raising the temperature and pressure of the continuously sampled liquor in an apparatus designed to simulate conditions thought to exist in the impregnation zone of the digester.

#### Liquor Sampling Site

Liquors for this study were taken from the suction of the makeup liquor pump in all cases but one, the exception being taken from the chip chute recirculation pump suction. The makeup liquor is usually pumped to the top of the

digester vessel where it is intermingled with the top recirculation liquor. The makeup liquor is composed of two parts -- fresh white liquor from storage and the overflow from the chip chute via the level tank, as shown in Fig. 21. The liquor in the chip chute is continually replenished by leakage into the chip chute from the top recirculation line at the high-pressure feeder and by condensate from the steaming vessel. The net flow from the top recirculation line to the chip chute is high -- on the order of several hundred gallons per minute. A small portion of the chip chute liquor enters the high-pressure feed pocket and is pumped to the top of the digester along with the chips. A larger portion of the chip chute liquor passes through the level tank and back into the makeup line. Thus, as shown schematically in Fig. 36, the top recirculation line, the chip chute recirculation line, and the makeup liquor line all continuously exchange liquors during routine digester operation.

The liquor entering the top of the digester vessel is similar to the liquor in the makeup liquor line, but is somewhat depleted in caustic concentration due to the low-temperature cooking that occurs in the chip chute and the top recirculation line. The volume of the top recirculation loop is relatively small compared with the capacity of the makeup liquor pump. Consequently, the liquor pumped into the top circulation loop will completely change-out the top recirculation liquor in a relatively short time -- a few minutes would be typical. In spite of this rapid replenishment of the top recirculation line with makeup liquor, some of the cooking chemicals -- particularly NaOH -- will be consumed before the chips and liquor enter the digester vessel at the top separator. The concentration of NaOH in the liquor at the top of the vessel may be only half that of the white liquor entering the process stream ahead of the makeup pump. The concentration of  $\text{Na}_2\text{S}$  will also be reduced relative to white



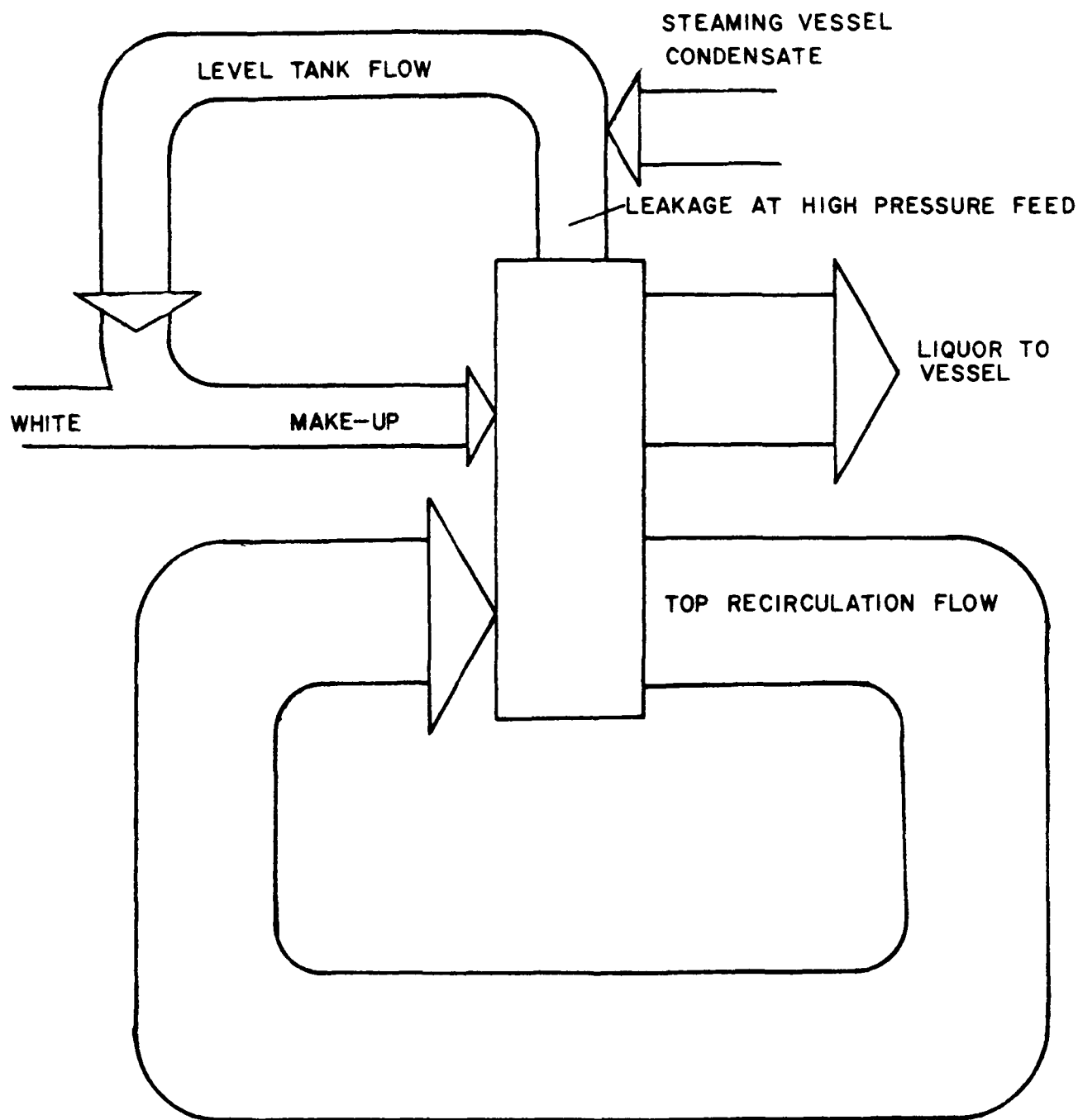


Figure 36. Schematic drawing of the interrelations of chip chute, makeup and top recirculation liquors in a Kamyr system.

liquor, but to a lesser degree since the sulfide does not participate as strongly in the low-temperature cooking process. Thus, the makeup liquors sampled in this program should be viewed as representing the upper bound on austic sulfide concentration that might enter a vessel; the actual concentrations in liquor entering the vessel will be somewhat lower.

#### Apparatus

The apparatus used for chemical sampling and for the in situ electrochemical studies is shown schematically in Fig. 27. The entire apparatus was assembled with stainless steel and Teflon materials of construction. The apparatus was connected to the drain valve at the suction of the makeup liquor pump via a Teflon-lined flexible metal hose. The liquors passed through the apparatus and were exhausted into the drain. A fine mesh screen filter was used to screen the incoming liquor, to prevent chip fines and other solids from plugging lines or affecting let-down regulator operation. Two testing chambers were used -- one at a low test temperature representative of top recirculation temperatures (200°F) and a second chamber for electrochemical testing at temperatures as high as high as 285°F (140°C). The second chamber was pumped to a pressure of 50-60 psi to suppress boiling of the liquors in contact with the liquor heaters. The chambers were heated at the bottom with cartridge heaters and along their length with heating tapes placed to maintain temperature uniformity. After departing the second chamber, the liquor was cooled to room temperature and let down to atmospheric pressure through a back pressure regulating valve. The liquor then passed through an automatic sampling system before being discharged to the drain.

The temperatures in the two chambers were controlled by a proportional temperature controller which adjusted the current applied to cartridge heaters

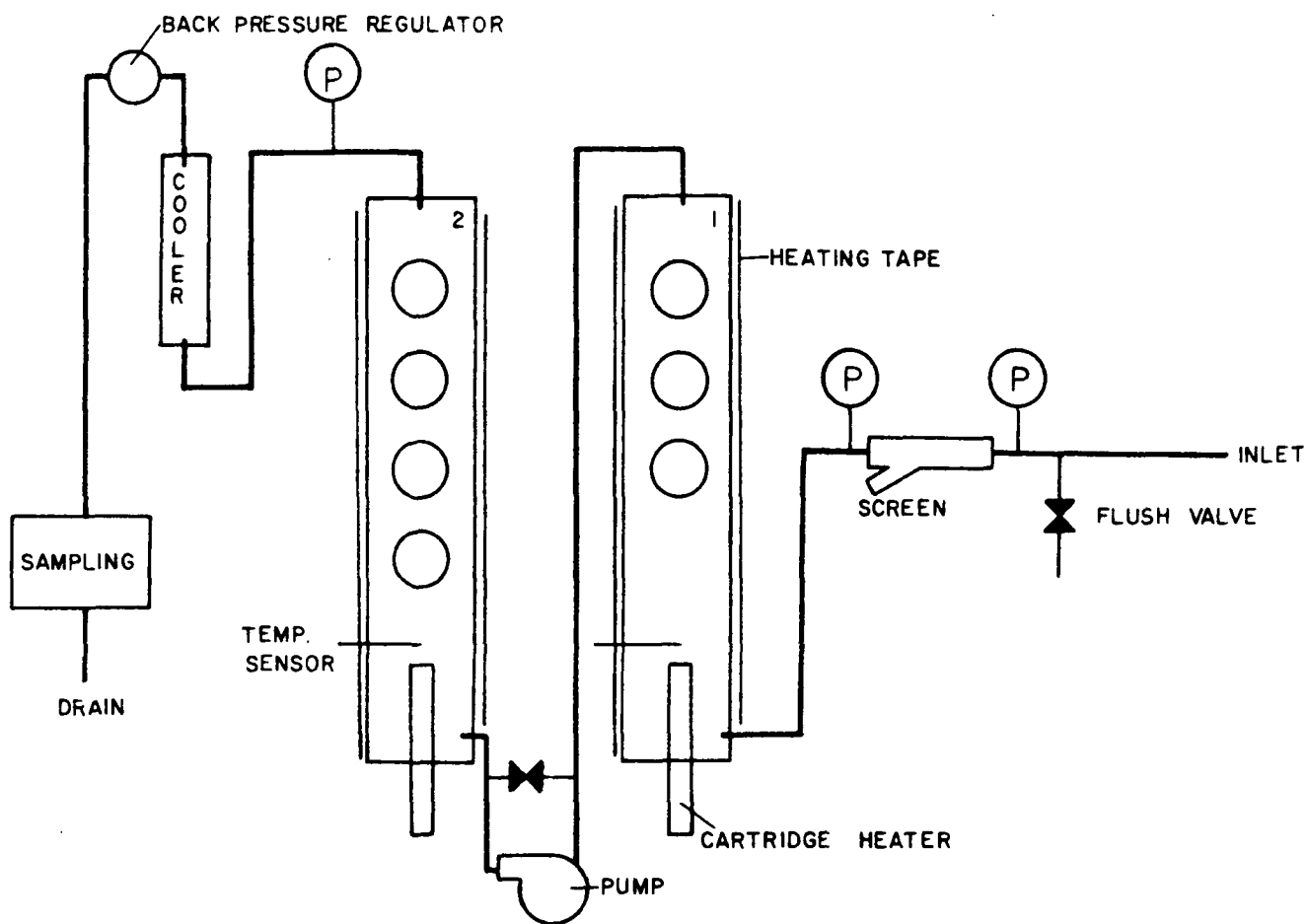


Figure 37. Schematic drawing of the apparatus used in the chemical and electrochemical analysis.

in the base of each chamber. Heating tapes positioned along the length of each chamber were excited with variable transformers to adjust for a constant temperature profile. Each of the chambers was completely insulated to minimize the heating load to that provided by a single 20 A, 110 VAC circuit that was routinely available in the mills.

The pressure in the second chamber was maintained by a high-pressure metering pump that also controlled the throughput of liquor through the apparatus. The metering pump selected had a throughput of 0.3 liters per hour. The pump employed was a valveless design which used a stainless steel plunger rotating in a matching graphite pump head. Frequent repairs were made to this pump because of the abrasive and corrosive nature of the liquors. After several early failures, the plumbing was modified with valves that permitted replacement of pump elements "on the fly"; a heat exchanger was also installed to cool the liquor before it entered the pump. A bypass line was also installed to allow purging of any air from the apparatus by rapid flushing with the liquor.

The filter was completely stainless steel with a stainless screen that passed 125-micron particles but retained most of the fines present in the liquors. The screen included a "Y" arrangement for flushing the screen, but manual cleaning was often required, as well. Pressure gages before and after the screen indicated plugging by their different readings.

The back pressure regulator was a Mitey-mite type of regulator which could be adjusted to control pressures in the range 0 to 100 psig by adjusting the pressurization of the top element. The regulator was protected from harmful temperatures by a heat exchanger in the inlet side.

The apparatus was set up to sample the liquors automatically in the event of a significant change in redox potential at a gold electrode in the first chamber. A schematic diagram of the sampling apparatus is shown in Fig. 38. A Potentiodyne Model 3010 Corrosion Rate Meter was utilized to detect the redox potential and to trigger an automatic sampling of the liquor if the redox potential of the liquor changed significantly during testing. If a shift occurred in the redox potential, a timing and logic circuit was energized to capture the liquor responsible for the change. Automatic valves were opened and closed to pass the liquor through the sampling bottle. After a period of time determined by the timing circuit, the position of the automatic valves was reversed, trapping the liquor sample in the sample bottle and bypassing the sample bottle with liquor subsequently leaving the apparatus. The timing circuit was adjusted so that the liquor causing the change in redox potential in chamber 1 was the same liquor trapped in the sample bottle.

Test electrodes were installed in the test chambers using the conventional Petrolite 3-electrode probes mounted in a modified pipe plug fitting. Three stations were used in test chamber 1 and four in test chamber 2. Each station was fitted with three electrodes -- a steel electrode, a silver/silver sulfide reference electrode, and a graphite counter electrode, with the exception of station 3, which had a gold foil electrode in place of carbon steel. The carbon steel electrodes were cylinders about 2.9 cm (1.125") high by 1 cm (.38") in diameter, with a  $9 \text{ cm}^2$  ( $1.4 \text{ m}^2$ ) surface area exposed to the liquor. The gold foil exposed about one half of this surface area. All electrodes were mounted to the threaded glass-to-metal seals in the electrode assembly using Hypalon gaskets. One base metal electrode and one weld metal electrode were exposed in chamber 1; two of each type were exposed in chamber 2.

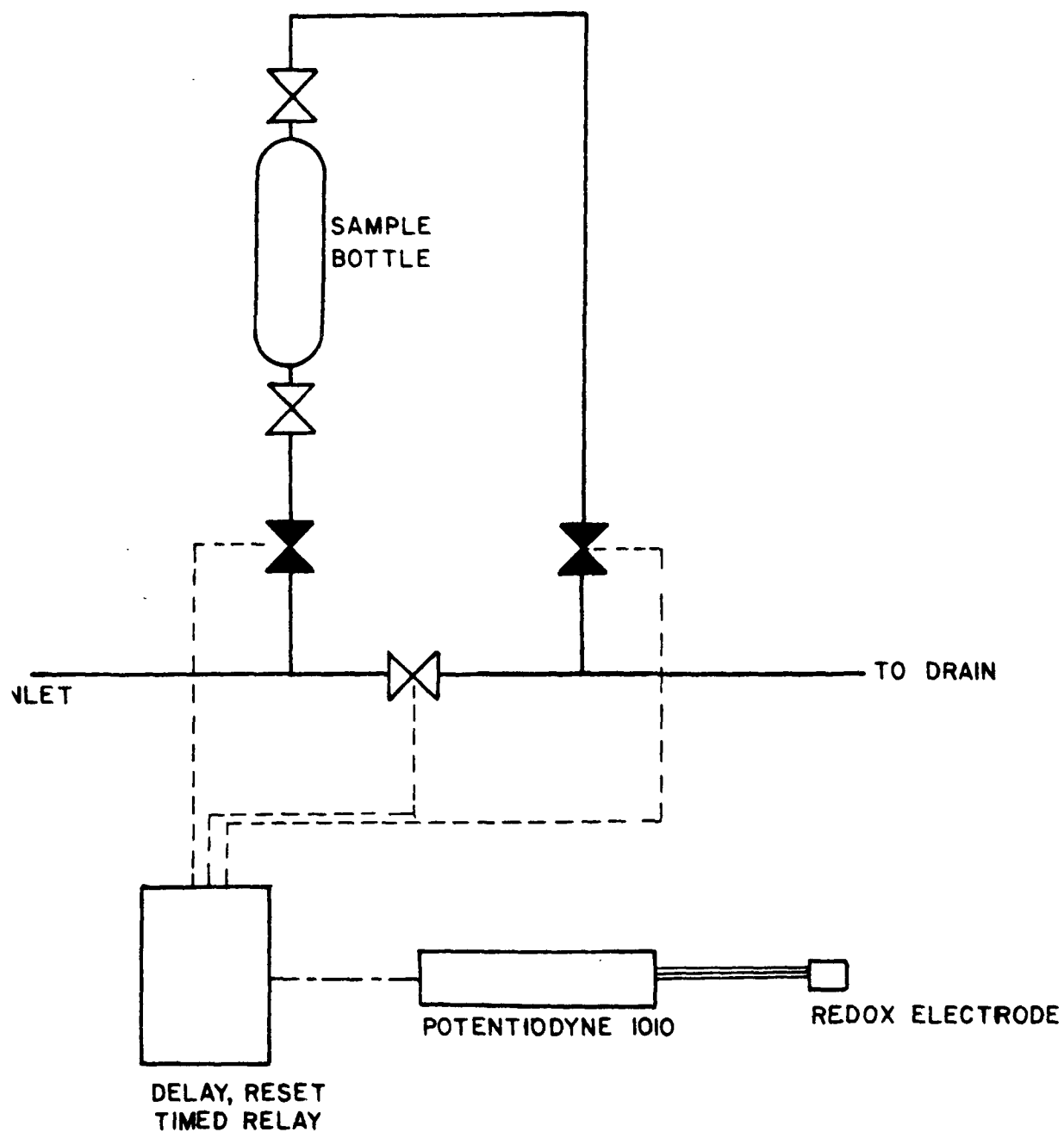


Figure 38. Schematic design of the automatic sampling apparatus.

The open circuit electrode potential and the corrosion rate of each of the test specimens were determined with a Potentiodyne Model 1010 Corrosion Rate Meter. This instrument automatically examined each of the electrodes in turn, first measuring the open circuit potential, and then measuring the corrosion rate using a linear potential method. In alternate scans, the corrosion rate was measured by alternate anodic and cathodic (10 mV) steps about the corrosion potential. Past experience has shown that the linear polarization measurements do not alter the open circuit potential in kraft liquors. The potentials and linear polarization curves were automatically recorded on a chart.

Polarization curves were also generated using the exposed electrodes and a Potentiodyne Analyzer. During these scans, the electrode station was temporarily disconnected from the Model 1010 instrument and connected instead to the Analyzer. Generally speaking, only the redundant electrodes in chamber 2 and the gold electrode were scanned before the test was about to be terminated, to insure that the act of taking polarization curves did not affect the spontaneous film formation at the steel electrodes. In those cases where the temperature of Chamber 2 was changed during the tests, the Analyzer was also used to clean the electrode surface by potentiostatting the specimen below the  $H_2$  evolution potential for 5 minutes at the new condition.

#### Electrode Materials

The test specimens used in the current program were manufactured from a weld that had been removed from a continuous digester that had shown severe cracking. The base metal was A516-70 and the weld metal was an E7018 multipass girth weld taken from the region of the lower cone transition. The specimens were oriented with the long axis of the specimen aligned along the rolling

direction of the plate and the longitudinal direction of the weld. Although tests on the HAZ were also proposed to the DCRC, these tests were not performed because HAZ material was not available from the specially welded plates that are yet to be welded for the DCRC program.

The reference electrodes chosen for this program were the Ag/Ag<sub>2</sub>S type suitable for direct immersion in the caustic cooking liquors. These reference electrodes were prepared by anodizing silver billets in a 100 g/L NaOH + 33 g/L Na<sub>2</sub>S solution for a few minutes. The reference potential of this electrode depends weakly on the sulfide concentration of the alkaline test media, but the changes were small over the range of sulfides encountered in the different liquors.

This reference electrode was calibrated versus a calomel reference electrode at temperatures ranging from room temperature up to 280°F (137°C), using makeup liquors from Mills 60 and 48. In this calibration, a double salt bridge with a wetted asbestos wick was used to isolate the calomel electrode from the poisonous effects of sulfide media. The contributions from liquid junction potentials and thermal junction potentials in this arrangement are unknown but thought to be small. The salt bridge arrangement is shown in Fig. 39. As shown in Fig. 40, the potential of the Ag/Ag<sub>2</sub>S was approximately -0.870 VSCE (-0.630 VSHE) in both of the liquors used. A stable reference potential was obtained within 30 minutes of immersion in the liquor. (Measurement of the potential of several Ag/Ag<sub>2</sub>S electrodes in test chambers 1 and 2 also showed that their potentials agreed within 1 mV in any liquor.) There was a slight tendency for the potential of Ag/Ag<sub>2</sub>S to increase as the temperature was raised from 70°F to 280°F, but the changes were small and scattered. In future discussions, the potential of Ag/Ag<sub>2</sub>S is standardized at -0.870 VSCE.



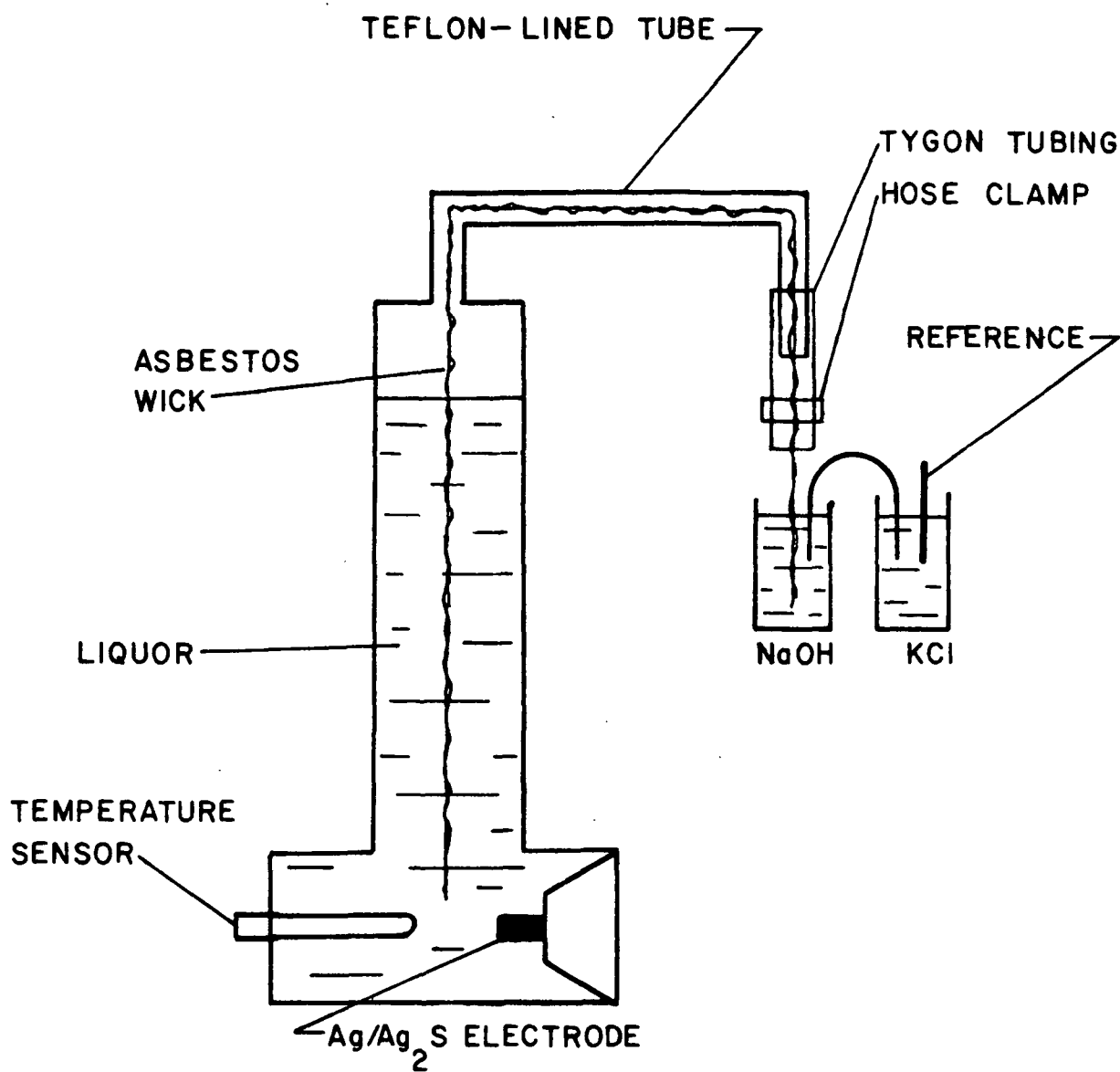


Figure 39. Apparatus used for calibration of the  $\text{Ag}/\text{Ag}_2\text{S}$  reference electrodes.

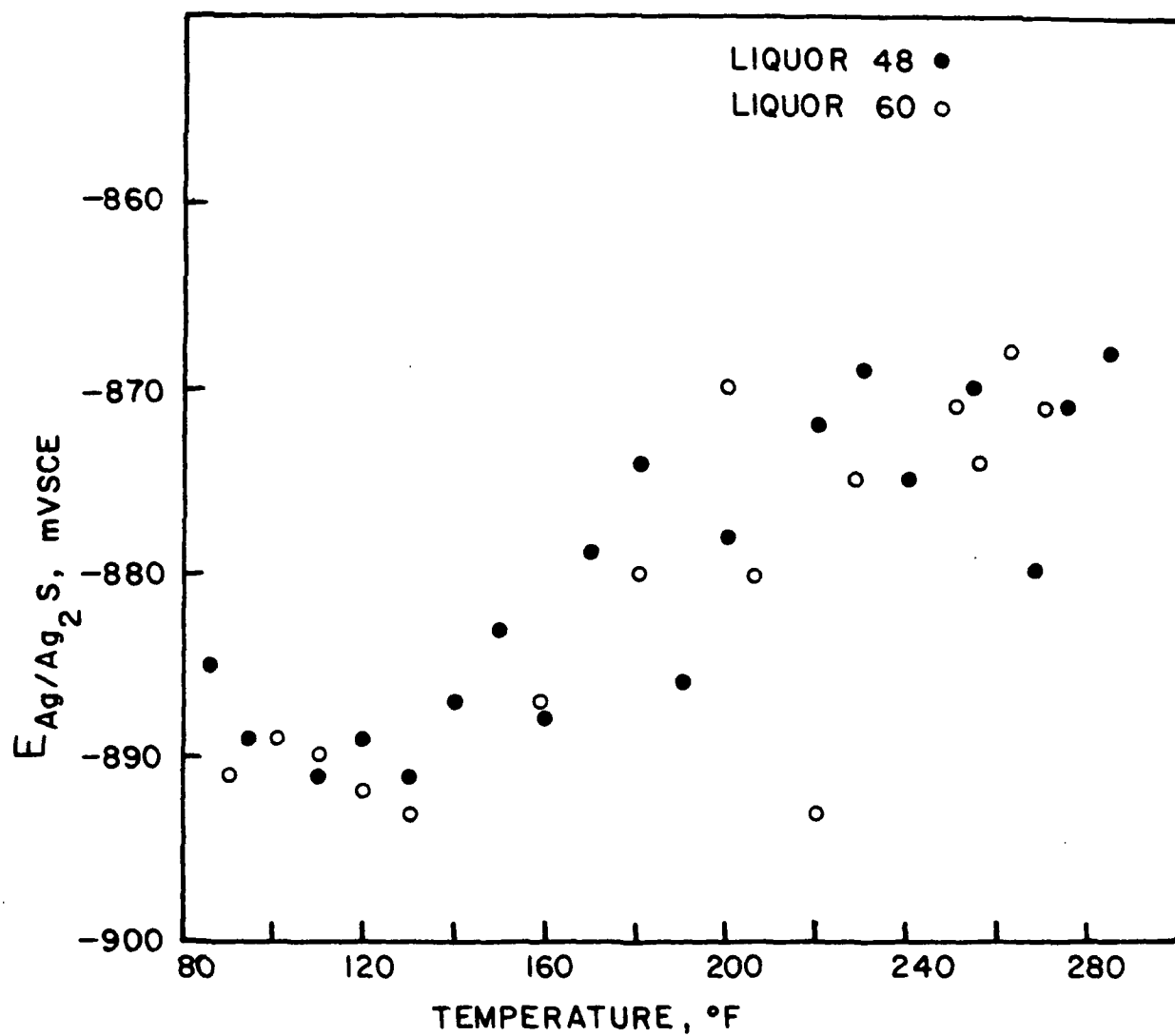


Figure 40. Calibration of the Ag/Ag<sub>2</sub>S reference electrode versus calomel.

### Grab Sampling

Although the apparatus was in place to allow sampling during any redox excursions, only one such excursion took place. Most sampling was done at periodic intervals during the mill visit, instead. Samples were taken by allowing the liquor to flow through a double-valved, stainless steel sample bottle until the gas in the bottle was completely purged. The double valves were then closed and capped with blank tube fittings, with care taken not to introduce air into the bottle. The sample bottles were then cooled to room temperature, packed in several plastic bags with absorbent vermiculite (in case of leakage), and air expressed to the Institute for chemical analysis. At the outset, care was taken to insure that specimens were analyzed within hours of collection. Repeated measurements on a single specimen indicated that the liquors were very stable if contact with air was avoided, and chemical analyses later in the program were done as convenient.

### Chemical Analysis

The liquors obtained in grab sampling were analyzed using a variety of techniques to ascertain chemical composition. Most of the tests conducted were focused on inorganic species, since the identification of organic species in these liquors is often difficult and uncertain. The sulfide concentration of the liquors was determined by a potentiometric titration with mercurous chloride and by the standard ABC titration. Good agreement between duplicate tests was obtained. The caustic concentration was determined using the ABC method and TAPPI standard T624; good agreement was obtained with the two methods. The sulfoxy compounds  $\text{SO}_3^-$ ,  $\text{SO}_4^-$ ,  $\text{S}_2\text{O}_3^-$  (thionates and other sulfoxy compounds were not found) and chloride were determined using ion chromatography. Carbonate concentration was determined using the ABC titration and ion chromatography;

good agreement was again observed. The presence of trace inorganic ions was characterized by emission spectroscopy and by energy dispersive X-ray analysis (EDAX) on dried solids in the scanning electron microscope (SEM).

Polysulfide measurements at first presented some difficulty because of the high color of the liquors and the interference with colorimetric methods for polysulfide analysis. The ultraviolet spectrophotometer method for polysulfide determination was affected by excessive absorption of the incident and scattered light by the colored solution. Similarly, the Mead Amalgam method for polysulfide analysis was confounded by problems with detection of a colorimetric endpoint for completion of a polysulfide reduction by sodium amalgam. A similar problem was encountered in the colorimetric endpoint for oxidation of polysulfide by  $\text{Na}_2\text{SO}_3$  according to the TAPPI standard method T624. In all of these cases, an initial procedure is the elimination of the characteristic polysulfide color by oxidizing or reducing the polysulfide compounds, and this color change could not be detected in the presence of chromophores in the liquors.

After repeated testing, it became apparent that (i) the reduction (or oxidation) of polysulfide was essentially complete after an exposure of the test solution to the amalgam (or  $\text{Na}_2\text{SO}_3$ ) for a few minutes at  $50^\circ\text{C}$ , and (ii) no conflicting reactions occurred unless the test solution was exposed to the amalgam (or  $\text{Na}_2\text{SO}_3$ ) for much longer periods. Thus, a reproducible change in the sulfide (or  $\text{Na}_2\text{S}_2\text{O}_3$ ) content of the liquor could be achieved, and a meaningful polysulfide measurement made by exposing the test solution to the reductant (or oxidant) for a few minutes without concern for any color change in the endpoint.

In the final analysis, the Mead Amalgam method was used to determine the polysulfide concentration of the sampled liquors, with a timed exposure to

the sodium amalgam for a few minutes at 50°C. Even this step did not completely resolve all of the problems with polysulfide determination, since the same test conducted on makeup liquor samples immediately after sampling a liquor caused a foaming of the liquor and meaningless results from the polysulfide analysis.

The only organic compounds specifically determined in the makeup liquors were the simple organic acids - formic, lactic, and acetic. The concentrations of these acids were determined using ion chromatography.

#### Procedure

Once the apparatus was set up at a mill site with the electrodes installed, a routine procedure was followed to start the electrochemical testing. The makeup liquor was flushed through successive stages of the apparatus to remove chip fines (ahead of the screen) and entrapped air bubbles beyond the screen. After the flushing procedure was completed, the pump bypass was closed and a stable flow rate was established through the apparatus. The temperature controllers for both chambers were then turned on, and a stable temperature profile was obtained by adjusting the proportional controllers and the variable transformer settings to the heating tapes. Once the system was operating as desired, cables from the two Potentiodyne corrosion rate devices were attached to the electrodes, and the routine for measuring potentials and corrosion rates began.

While the apparatus was operating, various tasks were completed including: (i) gathering samples and shipping them to the Institute from the nearest commercial airport, (ii) sampling liquids and conducting in situ measurements of sulfide and polysulfide, and (iii) running polarization curves on gold and the redundant electrodes in chamber 2. In practice, considerable effort was

required to keep all elements of the apparatus operating because of the high solids content of the liquors and their tendency to plug plumbing.

The specimens in chamber #1 were exposed continuously at a temperature in the range 195-200°F for the duration of the electrochemical testing effort at any mill. In chamber #2, the electrodes were usually passivated more quickly, and little additional information resulted from the continued exposure at the same temperature. Consequently, once the electrodes in the second chamber exhibited stable passivity for a day or two at 285°F, polarization curves were run on all electrodes, the temperature of the test chamber was lowered to 240°F, the electrodes were cleaned by evolving hydrogen gas on the surface, and the electrodes began a repassivation at the new temperature. In other cases, the temperature in chamber #2 was kept at 285°F to demonstrate that the passivity established at this temperature was indeed stable.

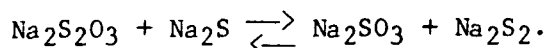
Cyclic polarization curves were run on the gold electrode and the duplicate electrodes in chamber #2 as the opportunity arose. Polarization curves were run using an inert gold electrode to differentiate redox reactions in the liquor from oxidation reactions involving dissolution. Cyclic polarization curves were run on all electrodes near the end of the tests in any chamber at the current temperature. In general, an anodic scan was conducted first to assess the extent of passivity (in the case of the steel electrodes) or the anodic redox reactions (in the case of gold and completely passivated steel). Thereafter, the potential was scanned to and held at  $-0.600$  V Ag/Ag<sub>2</sub>S to clean the surface by hydrogen evolution for 5 minutes. After this hydrogen cleanup, the potential was again scanned in the anodic direction to determine the electrochemical characteristics of the active metal surface. The scan rate used in all of the polarization curves was 1 mV/sec.

## RESULTS OF CHEMICAL ANALYSES

### White Liquor

At several mills, raw white liquor samples were taken at the outlet of the white liquor clarifier or storage tank for chemical analysis. The composition of the liquors is shown in Table X. No white liquors could be obtained from the 6th mill. The NaOH concentration ranged from 82 to 115 g/L, and the Na<sub>2</sub>S concentration ranged from 21 to 46 g/L, giving active alkalis in the range 91 to 118 g/L as (Na<sub>2</sub>O) and sulfidities ranging from 26 to 31% (AA basis).

The minor constituents of the white liquors (and the makeup liquors described subsequently) do not conform to the reported values for the equilibrium constant for the reaction



Haeglund and Roald (69) have reported an equilibrium constant for this reaction, K, with a value of  $1.6 \times 10^{-4}$ , where

$$K = \frac{[\text{Na}_2\text{SO}_3] [\text{Na}_2\text{S}_2]}{[\text{Na}_2\text{S}_2\text{O}_3] [\text{Na}_2\text{S}]}.$$

For the concentrations measured in these liquors, the equilibrium constant would be closer to  $1 \times 10^{-3}$ . The reason for the discrepancy is not clear.

The average data do not support a strong correlation between active alkali, sulfidity, and SCC susceptibility, as seen in Table X. To be sure, the 3 vessels that have experienced cracking are also the vessels that have the highest sulfidity, but mill 60 is nearly as high in sulfidity, yet no cracking is observed. Wensley (67) has suggested that mills with high sulfidity and low caustic are more susceptible to stress corrosion cracking; mills 143 and 48 do fulfill that condition, and these vessels have cracked. However, mill 137 has

TABLE X

RAW WHITE LIQUOR ANALYSES FOR SELECTED MILLS\* (g/L as chemical)

Mill Code	Sample Date	NaOH	Na <sub>2</sub> S	Na <sub>2</sub> CO <sub>3</sub>	Na <sub>2</sub> SO <sub>3</sub>	Na <sub>2</sub> SO <sub>4</sub>	Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub>	S <sup>o</sup>	Cl <sup>-</sup>
62 (NC)	<----- NA ----->								
137 (CR)	11/10	112.8a	40.2a	19.6a	2.8i	12.9i	6.1i	0.2m	
	11/10	107.4a	40.2a	19.7a					
	11/10	115.6a	39.6p						
143 (CR)	11/21	82.6a	45.9p	21.4a	3.0i	10.4i	5.8i	0.1m	1.17i
				19.3i					
48 (CR)	12/9	84.2a	37.9a	36.1a	3.9i	20.9i	7.8i	0.3m	1.51i
60 (NC)	12/19	102.0a	35.5a	30.0a	3.9i	23.6i	7.0i	0.3m	1.72i
			35.3p						
110 (NC)	1/7	95.4a	21.8a	26.8a				0.2m	
			20.8p	19.5i					
	1/10	95.4a	15.7a	21.4a					

\*i = ion chromatographic analysis  
a = acidimetric analysis  
m = Mead amalgam analysis  
p = potentiometric analysis



TABLE XI

RAW WHITE LIQUOR CONDITIONS\*

Mill Code	Cracking	NaOH	Na <sub>2</sub> S	AA	TTA	S
137	Yes	86.8 g/L	31.7 g/L	118.5 g/L	130 g/L	27.0%
143	Yes	64.0	36.5	100.5	112.4	30.0
48	Yes	65.3	30.0	95.3	116.4	31.5
60	No	79.0	28.1	107.1	124.7	26.2
110	No	73.9	16.9	90.8	106.5	18.6

\*g/L as Na<sub>2</sub>O.

cracked with an intermediate sulfidity and a high caustic concentration. Mill 60 has nearly the same sulfidity as mill 137, and an even lower NaOH concentration, yet this mill has remained immune from cracking. It must be emphasized, however, that the white liquor compositions shown above are one-time samples which may not represent the average (or the extreme) in white liquor conditions at these mills. These data, if representative of conditions existing during crack growth, do not support the contention that white liquor concentration has a dominant influence on caustic cracking susceptibility.

It is also clear that the minor constituents of raw white liquor do not control stress corrosion cracking susceptibility, at least if the samples described above are representative of average conditions. The sulfite, polysulfide, thiosulfate, and sulfate concentrations varied little from sample to sample, with no clear pattern distinguishing susceptible from nonsusceptible mills.

As an aside, it is interesting to note that the concentrations of white liquor constituents determined with alternative methods show relatively good

agreement, particularly for sulfide and carbonate analyses. To obtain the good agreement between the ABC acidimetric and other techniques, it was important to insure that the formaldehyde solution in the "B" step was at neutral pH before it was used to fix the hydrosulfide ion.

#### Cooking Liquors

The results of the chemical analyses of major and minor constituents in the cooking liquors (makeup liquor, in nearly all cases) are shown in Table XII. In the case of the organic-laden cooking liquors, some difficulty was experienced in obtaining good agreement among different test methods used to determine a given species concentration. There was no pattern to those occasions when, for example, the carbonate concentration in the ABC titration was unaccountably low compared with the more accurate ion chromatography value. In spite of these unexplained discrepancies, the overall agreement among various methods was generally very good.

Comparing Tables X and XII shows clearly that the makeup liquor is considerably different in composition from the raw white liquor because of the component added to the makeup liquor by recirculation through the level tank. Compared with white liquor, the cooking liquor has a lower NaOH and a higher  $\text{Na}_2\text{CO}_3$  concentration, as might be expected from the low-temperature cooking thought to occur in the recirculating liquor lines. The sulfidity of the cooking liquor is slightly lower than the raw white liquor due to the modest consumption occurring during the low-temperature cooking.

Once again, it is very difficult to detect a correlation between the concentration of major and minor inorganic species in the cooking liquor and the susceptibility of the vessel to cracking. Indeed, the cooking liquors are

TABLE XII  
MAKEUP LIQUOR ANALYSES FOR SELECTED MILLS\* (g/L as chemical)

Mill Code	Sample Date	NaOH	Na <sub>2</sub> S	Na <sub>2</sub> CO <sub>3</sub>	Na <sub>2</sub> SO <sub>3</sub>	Na <sub>2</sub> SO <sub>4</sub>	Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub>	S <sup>o</sup>	Cl <sup>-</sup>	Remarks
62 NC	10/15	60.3a	25.2p		6.2i	5.0i	5.4i	0.2m		Chip Chute Liquor
62 NC	10/15		25.1p							Chip Chute Liquor
62 NC	10/25	70.4a	19.5p	21.4i	3.3i	4.7i	5.5i	0.2m		Chip Chute Liquor
62 NC	10/26		20.4p		4.3i	4.9i	4.1i	0.1m	3.46i	Chip Chute Liquor
62 NC	10/28	56.1a	17.7a	25.1a						Chip Chute Liquor
137 CR	11/3	78.5a	28.1a	22.2a	6.3i	12.1i	7.3i	0.1m		
137 CR	11/3		31.9p	21.4i						
137 CR	11/3		32.9pm							Hardwood
137 CR	11/4		32.6pm							Hardwood
137 CR	11/5	75.8a	31.2pm	23.8a	2.7i	11.4i	7.3i		1.23i	Softwood
137 CR	11/5		32.3p	22.0i						Softwood
137 CR	11/5		23.7a							Softwood
137 CR	11/6		36.2pm							Softwood
137 CR	11/7		29.5pm							Softwood
137 CR	11/8		32.6pm							
143 CR	11/16	57.0a	31.4a	20.9a	3.0i	4.9i	6.2i	0.1m		
143 CR	11/16	54.1a	31.4p	18.2i						
143 CR	11/16		41.9pm							
143 CR	11/17		40.7pm							
143 CR	11/18		36.7pm						0.91i	
	11/21	55.4a	17.4a**	21.0a	3.6i	8.6i	7.3i	0.1m		
			33.8p							
48 CR	12/3		19.4pm							
48 CR	12/5	50.3a	27.4a	29.6a	3.6i	8.7i	21.6i		0.97i	
48 CR	12/5		25.7p							
48 CR	12/5		26.1pm							
48 CR	12/6		27.0pm							
48 CR	12/8	35.0a	16.6a	24.3a	4.3i	7.3i	8.7i		0.75i	Upset condition
48 CR			15.7p							
60 NC	12/13	76.4a	33.8a	32.3a	3.9i	15.1i	9.2i		1.69i	
60 NC	12/13		33.8p							
60 NC	12/15	70.6a	23.4a	18.6a	3.1i	20.5i	7.2i		1.11i	Synthetic Liquor
60 NC			23.9p							Synthetic Liquor
60 NC	12/19	78.5a	22.5a	25.1a	3.2i	18.0i	5.5i		1.45i	Synthetic Liquor
			27.9p							
110 NC	1/7	61.5a	15.3a	31.1a	3.1i	6.4i	5.5i	--	3.97i	
	1/7		13.0pm	16.7i						
	1/11	55.0a	16.9a	21.9a						

\* a = acidimetric, p = potentiometric, i = ion chromatography, m = Mead amalgam, pm = mill site potentiometric  
\*\* questionable data

perhaps more uniform in composition than the raw white liquors, apparently due to a "buffering" action that accompanies the low-temperature cooking in recirculation lines. The absence of a strong correlation between inorganic liquor chemistry and cracking is especially evident in the results for mill 60, which has concentrations of most species in the range found in those vessels that have cracked.

Caution is again required in the broad interpretation of such a small sample of cooking liquor. In most cases, only one week was spent at the mill, and only a small number of samples were taken. Insofar as these samples represent the normal cooking liquor chemistry, that chemistry does not appear to control cracking susceptibility. This cautionary note is especially relevant in view of the labile nature of the liquor chemistries. Relatively large changes are seen in the day-to-day liquor chemistries presented in Table XII, and it is clear that the "average" composition of a liquor may have little physical meaning when such large fluctuations are possible.

On the other hand, it is interesting to note that significant changes in mill operation have only a small effect on liquor chemistry. For mill 137, for example, swings between hardwood and softwood pulping have little effect on cooking liquor composition. Similarly, a period of operation with synthetic liquor also has only a small effect on liquor composition. As will be seen later, these changes in operation had little effect on the electrochemical behavior of steel immersed in cooking liquors.

One nonroutine event that had a significant impact on both the chemistry and electrochemistry of cooking liquors took place at mill 48 on December 8. At 10 AM, an upset condition occurred as a result of screen cleaning in the

level tank recirculation line. Large amounts of live steam were apparently directed into the line, with the result that the liquors were considerably diluted. A sample taken at that period showed a much more dilute liquor than had been detected previously at the mill. As will be seen later, this change also affected the electrochemical behavior of steel immersed in the makeup liquor, as well.

The results of three special analyses of cooking liquors are displayed in Table XIII. The first is a summary of five ion chromatographic analyses performed on a single sample of chip chute liquor, taken in five separate sample bottles kept sealed until the analysis was begun. The first analysis took place a few hours after the sample was taken and shipped to the Institute for analysis. The last analysis took place 120 hours after the sample was taken. There is no trend to the scatter in composition of the sulfoxy compounds, indicating that the sampling procedure was adequate. Furthermore, it was apparent that no changes in liquor chemistry were likely during shipment of the liquors from remote mills by air express.

The data from mill 60 presented in Table XIII address the uncertainty about the composition of the top recirculation liquor as it compares with makeup liquor. Liquor was obtained from the top recirculation line at mill 60, using leakage from the drain valve in the line. Liquor was flowing from a faulty weld adjacent to the valve at a steady drip rate. Some flashing was occurring as the liquor was depressurized, but since the liquor in the line was close to the atmospheric boiling temperature, the amount of flashing was small. This top recirculation liquor was gathered and analyzed and found to have the composition shown in the table. The concentration of the inorganic chemicals in this liquor

TABLE XIII

SPECIAL LIQUOR ANALYSES (g/L as chemical)

Mill Code	Date	NaOH	Na <sub>2</sub> S	Na <sub>2</sub> CO <sub>3</sub>	Na <sub>2</sub> SO <sub>3</sub>	Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub>	Na <sub>2</sub> SO <sub>4</sub>	S <sup>o</sup>	Cl <sup>-</sup>	Remarks
62 (NC)	10/15				4.9i	5.1i	5.3i			3 hrs. after sample 24 48 96 120
					6.8i	5.8i	5.0i			
					4.1i	4.7i	4.1i	0.2m		
					7.0i	5.7i	5.2i	0.2m		
					8.4i	5.7i	5.2i		3.46	
60	12/19	91.2a	33.8a	40.5a 44.4i	3.9i	14.9i	25.7i		1.97	Top Recirculation (Flashed)
	12/19	78.5a	22.5a	25.1a 25.2i	3.2i	5.5i	18.0i		1.45	Makeup
	12/19	102.0a	35.5a	30.0a 31.1i	3.9i	7.0i	23.6i		1.72	Raw White
	11/21	82.6a	45.9p 45.0a	19.3a	3.0i	5.8i	10.4i		1.17i	0.1 White
143 (CR)	11/21	55.4a	33.8p	21.0a	3.6i	7.3i	8.6i		0.9i	0.1 Makeup
	11/21	19.9a	23.3p	26.3	2.7i	5.4i	4.6i		0.79	- Bottom Circulation
	11/21	14.1a	24.2a	24.1a	3.8i	5.4i	3.7i		0.50	- Trim
	11/21		20.3p 19.0a							

\*i = ion chromatographic analysis  
a = acidimetric analysis  
m = Mead amalgam analysis  
p = potentiometric analysis

was similar to, but somewhat higher than, that of the makeup liquor, which is attributed to the evaporation of a portion of the water originally in the sample. It is noteworthy that the proportions of NaOH, Na<sub>2</sub>S and Na<sub>2</sub>CO<sub>3</sub> are virtually identical to those found in the makeup liquor sample taken at the same time.

The third set of data in Table XIII, gathered at mill 143 on November 11, also addresses the question of degree of cooking in the impregnation zone. One of the liquors taken on that date was from the bottom circulation line that carries chips from the bottom of the impregnation vessel to the top of the digester. This liquor is thought to be representative of the liquor present at the bottom of the impregnation zone of one-vessel digesters and will indicate the degree of cooking and the composition of the liquor at that location. The second liquor, taken from the trim recirculation line, is essentially representative of that in the cooking zone of the vessel. It is clear from these data that a large amount of cooking chemical is consumed in the impregnation zone before high temperature cooking has begun. Less than half of the active alkali remains after the impregnation zone is traversed. The (room temperature) pH at the bottom of the impregnation zone has dropped to 11.9 for both bottom circulation and trim liquors. Once again, although considerable amounts of cooking chemicals have been consumed, only the carbonate shows an increase in concentration among the inorganic compounds.

The implications of these results regarding the effects of chemical composition on cracking susceptibility are noteworthy. It appears that the changes in chemical composition of the liquor as it passes from the top of the digester to the cooking zone are much larger than any changes in liquor from

mill to mill. Every vessel will experience a range of caustic and sulfide concentrations along the length of the vessel. If a critical liquor composition was instrumental in causing cracking, the vessels with a high concentration of the damaging species should be cracked at levels closer to the cooking zone. Conversely, mills with lower concentrations of damaging species would be expected to reach the critical concentration at higher elevations, since less chemical has to be removed by cooking. However, there is no evidence that such a distribution of cracking occurs -- the same welds are cracked in most vessels regardless of chemistry.

#### Trace Elements

Trace contaminants were also determined in the liquors taken at each mill site, to determine if trace metals or other trace elements in the liquors can be correlated with cracking susceptibility. Two types of analyses were performed. The samples were reduced to sulfated ash and analyzed in the emission spectrograph; in addition, small quantities of liquors were evaporated to salt and analyzed using the EDAX analyzer in the scanning electron microscope. The emission spectrographic results are summarized in Table XIV. Silicon was present at a few hundred parts per million, whereas Fe, Al, Cu, Ca, and Mn were present in concentrations of only a few parts per million. Nickel and mercury -- potential contaminants from caustic manufacturing -- were not found. Two typical EDAX spectra are shown in Fig. 41 and 42 for liquors from susceptible and non-susceptible mills. While peak heights in these spectra are not exactly proportional to the concentration of elements present, they do provide a qualitative picture of the species which are present. In addition to major Na and S peaks, there is evidence of some quantity of potassium, silicon, chlorine and aluminum. There is no difference in these trace elements, or those detected in the emission



TABLE XIV  
TRACE CONSTITUENTS (g/L) BY EMISSION SPECTROGRAPH

Mill Code	Date	Ash	Si	Mn	Fe	Al	Ca	Cu	Ag*	V	Remarks
62	10/26	185 g/L	0.14 g/L	0.022	0.016	0.16	0.065	0.012			Chip Chute Liquor
137	11/5 11/10	232 312	0.2 0.40	0.008 <0.005	0.040 0.029	0.016 0.026	0.112 0.13	0.003 0.004			MLP Liquor White Liquor
143	11/21	206	0.32	0.011	0.033	0.070	0.080	0.013			MLP Liquor
48	11/21	274	0.41	0.006	0.027	0.12	0.10	0.005			White Liquor
48	12/5	211	0.31	<0.004	0.052	0.094	0.074	0.007	0.012		MLP Liquor
60	12/9	297	0.35	0.006	0.033	0.11	0.08	0.018			White Liquor
60	12/19	313	0.33	0.014	0.072	0.026	1.10	0.004			White Liquor
60	12/12	269	0.26	0.19	0.082	0.025	0.29	0.048	0.005		MLP Liquor
110	1/7	195	0.29	0.012	0.026	0.045	0.11	<0.001		0.11	MLP Liquor
	1/7	270	0.33	0.012	0.027	0.085	0.087	<0.001		0.11	White Liquor

\*Apparently due to the Ag/Ag<sub>2</sub>S electrode.

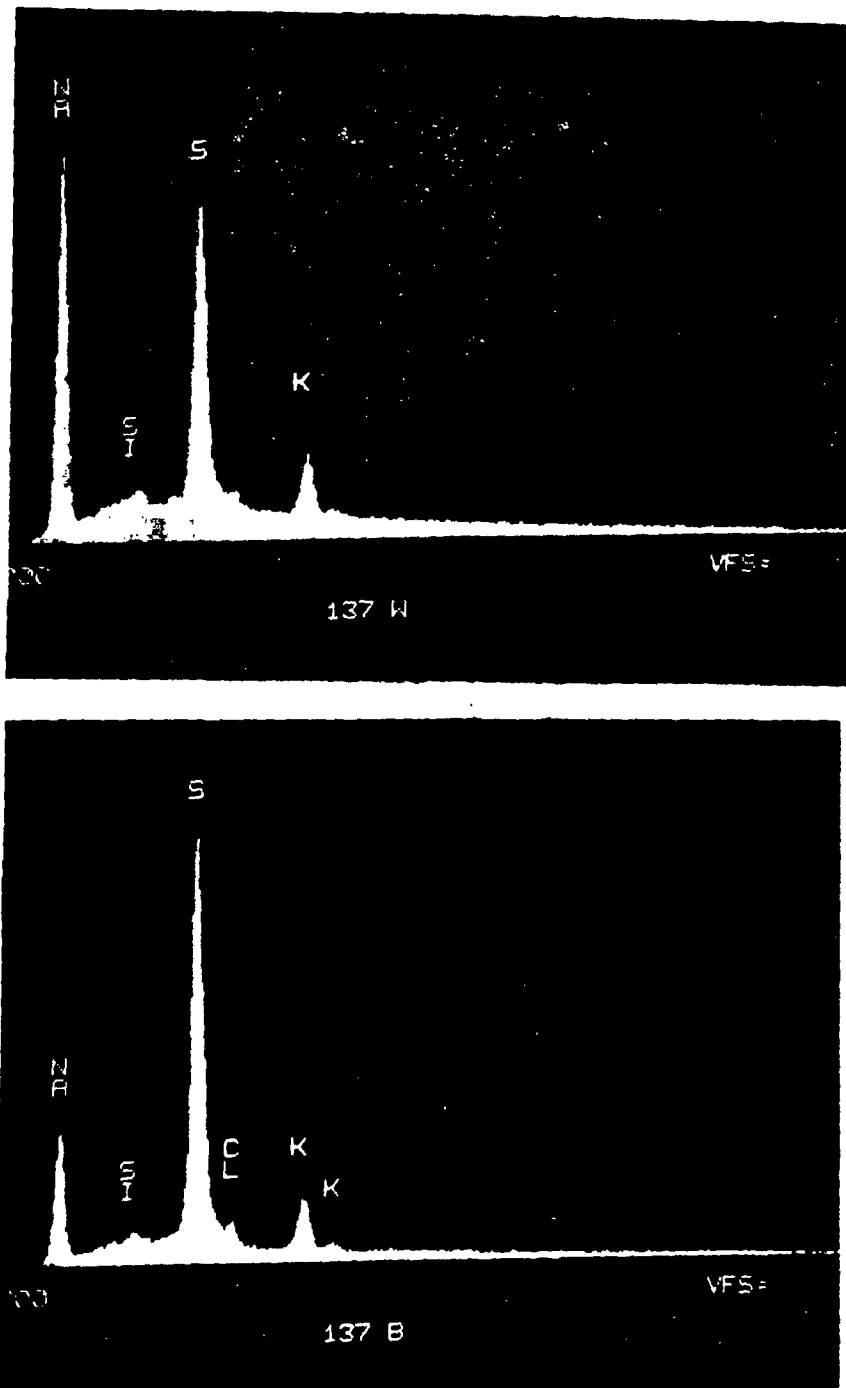


Figure 41. EDAX spectra for white and makeup liquors from mill 137, a susceptible mill.

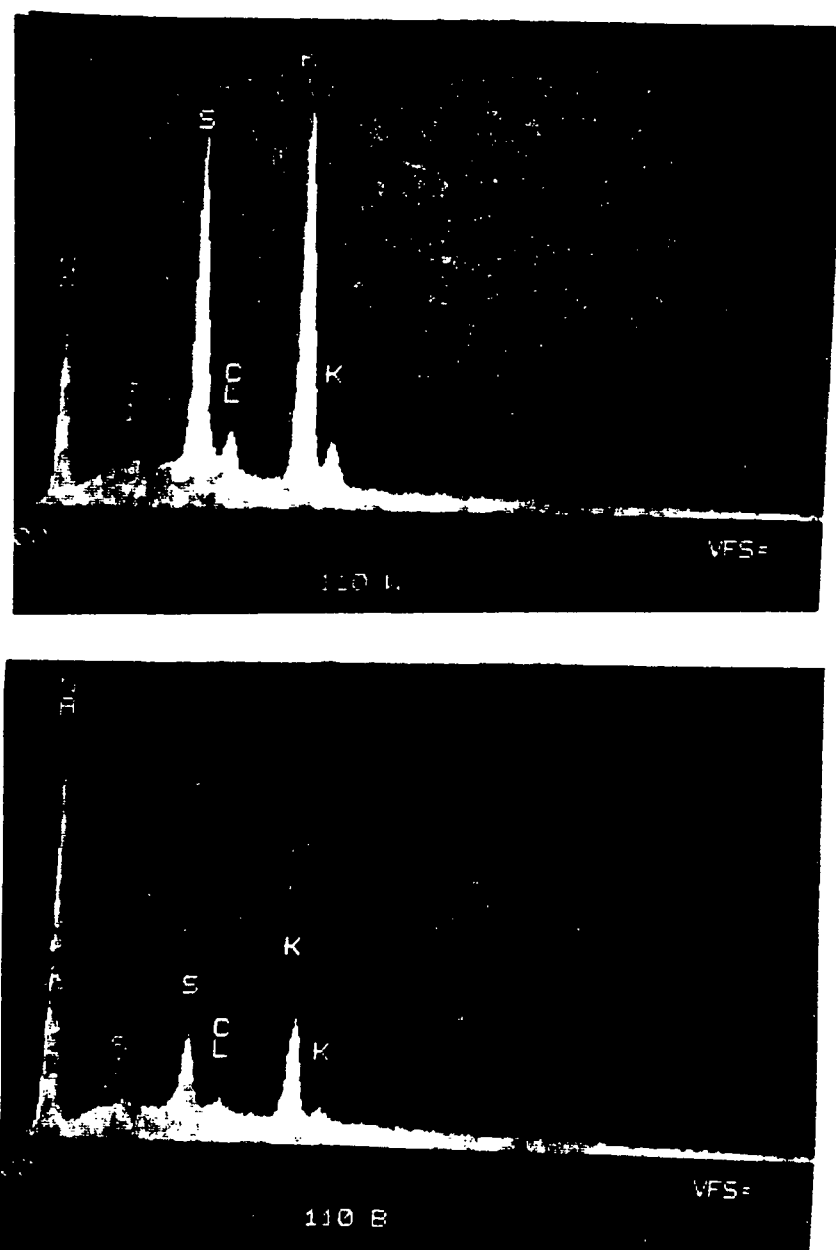


Figure 42. EDAX spectra for white and makeup liquors from mill 110, a non-susceptible mill.

spectra, that can be related to cracking susceptibility at the six mills considered.

### Organic Species

Since the analysis of organic constituents in these liquors was thought to be a Herculean task requiring considerable method development and calibration, no substantial effort was made to characterize the organic species present in the liquors. In a few cases, the ion chromatograph was used to determine the concentration of three organic acids in makeup and white liquors. The results, as shown in Table XV, indicate that the concentration of acetic, formic, and lactic acids present in the liquors increases as low-temperature cooking proceeds, as might be expected. The large quantity of organic acids present in the bottom circulation liquor would indicate that these species -- and probably a multitude of related products of low-temperature cooking -- will be present in the liquor at the site of cracking in concentrations of 1 to 5 grams per liter.

Table XV

#### ORGANIC ACIDS IN LIQUORS (g/L as chemical)

Mill Code	Sampled	Lactic Acid	Formic Acid	Acetic Acid	Remarks
62	10/20	0.89	0.88	1.65	Chip Chute
137	11/3	0.39	0.26	3.19	Makeup Liquor
	11/5	1.29	1.24	4.06	Makeup Liquor
	11/10	0.00	0.00	0.00	White Liquor
143	11/16	0.56	0.42	2.05	Makeup Liquor
	11/21	0.77	0.57	1.09	Makeup Liquor
	11/21	0.00	0.00	0.00	White Liquor
	11/21	5.00	4.83	5.21	Bottom Circulation Liquor
	11/21	5.67	5.28	4.61	Trim Liquor

### Summary

In spite of an intensive analytical effort, no correlations have been found which relate SCC susceptibility to major, minor, or trace constituents of cooking liquors. Several explanations fit these observations, including the following possibilities.

- (i) There is no correlation between cracking and cooking liquors in normal circumstances.
- (ii) There is a correlation between cracking and cooking liquor characteristics, but the damaging conditions are not always present and were absent when the current sampling was done.
- (iii) There is a correlation between cracking and cooking liquor characteristics, but the damaging species was not considered (organics?) or the correlation is not simple.

As will be seen in the next section, (i) is the most likely explanation.

## ELECTROCHEMICAL BEHAVIOR IN COOKING LIQUORS

### Rest Potentials

Both the weld metal and the base metal were initially active when immersed in the caustic cooking liquors, with an initial potential on the order of -150 mV Ag/Ag<sub>2</sub>S (-1.02 VSCE). This potential is typical of that for bare steels exposed to caustic solutions in the absence of a significant concentration of oxidizing species (2,4,42). There were no consistent differences in the potentials of weld metal and base metal; small differences are attributed to small differences in surface condition. The redox potential of the gold electrode was rapidly stabilized in the vicinity of +150 to 170 mV Ag/Ag<sub>2</sub>S and

remained steadfast at this potential unless the electrode was polarized with the potentiostat. If the gold redox electrode was disturbed, a half-hour transient would occur as the electrode returned to its normal redox potential.

As soon as the carbon steel electrodes were immersed in the cooking liquor, the rest potentials began to drift upward as observed by Humphries and Parkins (42), Harrison et al. (41) and Reinoehl and Berry (32) for tests in pure caustic (See Fig. 18). The rate of upward drift in potential is shown for several electrodes in a cooking liquor at two temperatures in Fig. 43. The rate of upward drift is dependent on temperature, with a more rapid rise at 284°F than at 200°F. The rate of drift of the open circuit potential does not depend on whether the electrode is a base metal or a weld metal. The galvanic effect of coupling weld metals and base metals should be small, since the potential difference between weld metal and base metal is only a few millivolts.

The upward drift of the potential ceased as the potential of the steel approached that of the gold redox electrode. In some cases, particularly at the lower temperatures, the steel electrode did not quite reach a stable rest potential in the time available for exposure. The rest potential for both base metal and weld metal usually stabilized at about -90 mV Ag/Ag<sub>2</sub>S (-0.060 VSCE) at 200°F. The corresponding rest potential at 280°F was +50 mV Ag/Ag<sub>2</sub>S (-0.820 VSCE). Some variations were observed from mill to mill, generally attributed to upset conditions in the apparatus (pump failure) preventing the attainment of a stable rest potential. In mill 110 the rest potentials were a little higher than in the other mills (~ + 150 mVSCE), perhaps because of the relatively low sulfide content at this site.

Examination of partially passivated specimens after rinsing revealed electrodes covered with patches of a blue-black film thought to be magnetite.

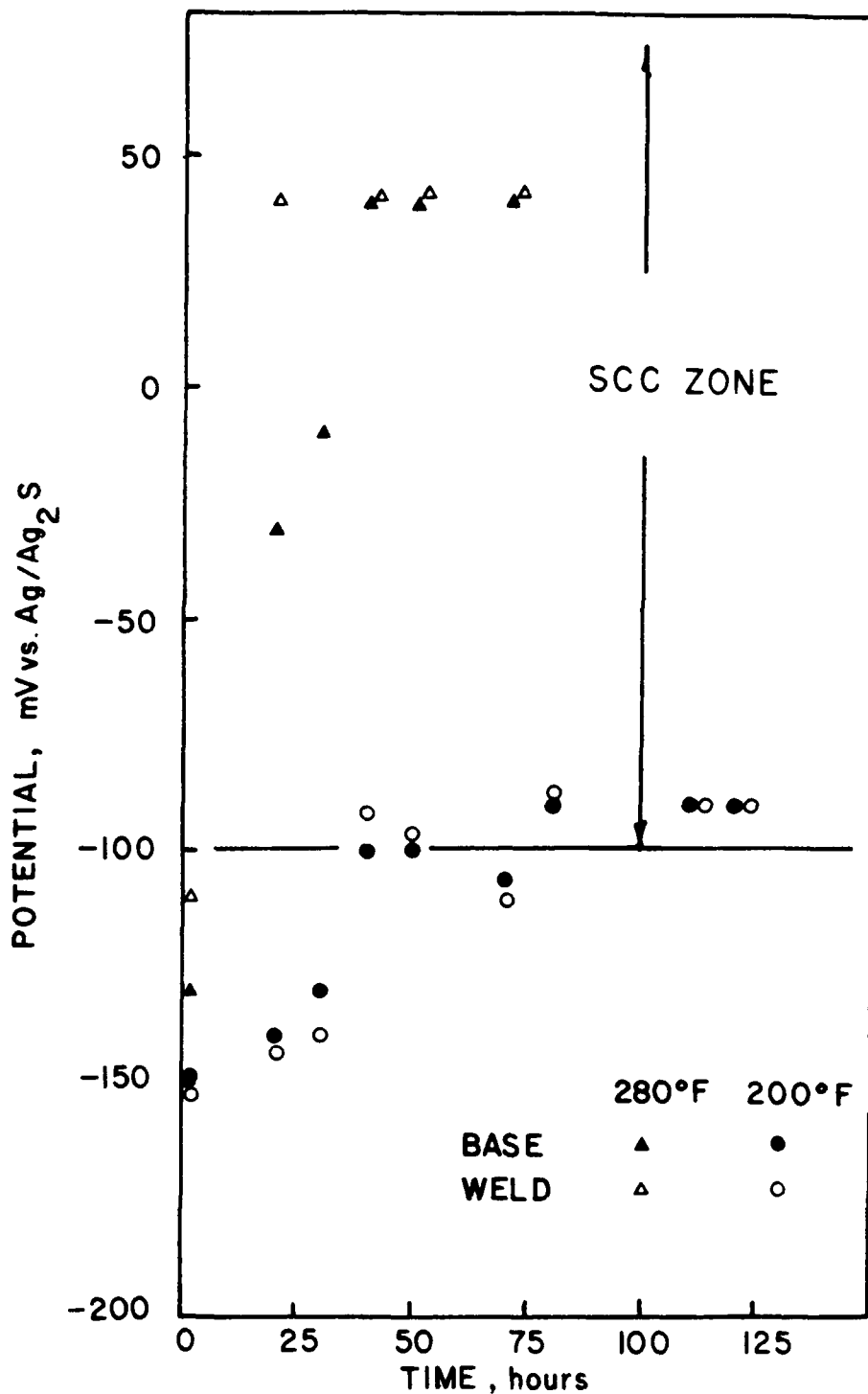


Figure 43. Upward drift of the rest potential of steels immersed in cooking liquors. The SCC zone shown is for carbon steel in NaOH/Na<sub>2</sub>S mixtures at 90°C.

The rest of the surface was covered with a reddish-brown corrosion product indicative of active corrosion in the caustic before exposure to the air. The electrodes achieving a stable rest potential were covered with a thick black deposit over an adherent black film. The rise in open circuit potential is associated therefore with a gradual passivation of the electrodes by the formation and growth of patches of magnetite. A fully passivated metal would be covered with a nonprotective FeS deposit on top of a protective magnetite deposit.

The film formed in the cooking liquors was very fragile and could be destroyed by any of several different events. Impressing a potential below the hydrogen evolution potential would reactivate the electrodes by removing the film, restoring the  $-200 \text{ mV Ag/Ag}_2\text{S}$  rest potential and initiating a renewal of the upward drift of potential. Similarly, upset conditions in the apparatus (with loss of temperature in a chamber because of blockage, for example) could also activate the samples by damaging the protective film.

In one interesting series of events, the screen cleaning event at mill 48 that caused a marked drop in the concentration of makeup liquor chemicals also caused a reactivation of partially passivated specimens in both high- and low-temperature chambers. Potentials in the high-temperature chamber dropped from  $+40$  to  $-195 \text{ mV}$  during this excursion, for example. This was the only active-passive reversal associated with the liquor chemistry observed in any of the six mills. All other transitions were attributed to upsets in the flow of liquor through the test apparatus by blockage with fines, or potentiostatic manipulations of electrode potential.

It is most interesting to note that the stable rest potential achieved by the base metal and weld metal electrodes at all of the mills lies within the



potential range where SCC was observed in laboratory tests in simulated white liquor. Singbeil and Tromans (54,55) report SCC at 200°F only in the potential range  $\pm 50$  mV about  $-0.88$  VSCE (i.e.,  $-0.83$  to  $-0.93$  VSCE). Within the resolution of the tests, the stable rest potential at 200°F was found to be in this range in actual cooking liquors at both temperatures tested. Thus, the stable rest potential in cooking liquors at both immune and susceptible mills comes to reside in that narrow regime where caustic cracking has been observed in the laboratory.

It is reasonable to conclude, based on the potentials achieved, that all of the liquors tested would support caustic cracking processes if a carbon steel was subjected to an appropriate tensile stress. Apparently, immune mills have been immune, not because of some ideal liquor chemistry, but rather because one of the other necessary conditions for caustic cracking -- high tensile stresses, access of liquor to the metal through scale buildup, a susceptible metallurgical structure -- was not satisfied.

In light of this observation about the virulence of liquors at all mills surveyed, the experience with SCC at stitch welds becomes more meaningful. In many mills that were otherwise immune to cracking (and graded as having D type immunity), the non-stress-relieved stitch welds attaching dummy plates and screen plates to the vessel were cracked. This is a very common occurrence, considered more of a maintenance item than a real concern at most mills. However, even these welds of low quality would not be cracked unless the liquor was conducive to SCC even in the otherwise immune vessels, as described above. This suggests that the mills which have not exhibited cracking have cooking liquors which would crack carbon steels if all other conditions of stress, metallurgical structure, etc., were satisfied.

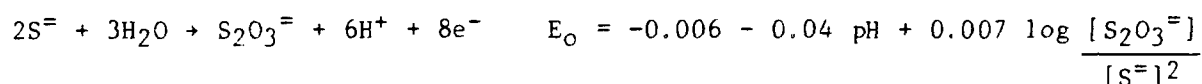
Experience with welded carbon steel piping in the liquor circulation lines also supports the concept of a critical potential range for cracking. Cracks have not been reported in any of these non-stress-relieved pipe welds, even though they are exposed to much the same liquors as the top of the vessel. It is likely, as has been observed for other situations involving flow rates of active-passive media, that the high flow rate will cause the piping welds to remain active and not achieve a rest potential in the critical regime for cracking. If the potential is active and outside of the range required for caustic cracking, no cracking should be observed in pipe welds.

#### Polarization Curves

The polarization curves generated on gold and steels in liquors at the different mills demonstrate why the rest potential resides in the cracking range, rather than continuing to rise beyond the danger zone as shown for exposures to pure caustic (Fig. 18). Apparently, an oxidation reaction involving unknown species in the liquor will occur on electrodes at potentials noble to the redox potential of gold. In fact, this oxidation is probably instrumental in establishing the redox potential of gold in these liquors.

As shown in Fig. 44, the anodic polarization curves for the gold electrode are virtually the same at all of the mills and at different times at the same mill. Since gold is inert, the oxidation reaction occurring on the gold surface must involve the oxidation of some species present in sufficient quantity in the liquor. According to Biernat and Robins (68), several reactions involving sulfur compound oxidation are possible at the potentials of interest, but uncertainty about the concentration of species present, the activity coefficients of these species, their overpotentials, and the hydrodynamics at the

redox electrode prevent identification of the oxidation reaction occurring at +200 mV Ag/Ag<sub>2</sub>S. Some possible reactions include:



Whatever the actual reaction, raising the potential of gold above 200 mV Ag/Ag<sub>2</sub>S will only occur when a cathodic reaction is available that can consume 100 mA/cm<sup>2</sup> of electrons liberated by this liquor oxidation reaction.

The same oxidation of some species in cooking liquor apparently occurs on the surface of steel electrodes that have been rendered more or less inert by formation of a passive film. As shown in Fig. 45, passivated steel and gold show the same anodic polarization curve above +150 mV Ag/Ag<sub>2</sub>S, indicating that the same oxidation reaction occurs on both metals.

If a passivated steel specimen is to continue its spontaneous upward drift in rest potential beyond the anodic peak at 200 mV Ag/Ag<sub>2</sub>S, some cathodic process must be available to consume the ~ 100 mA/cm<sup>2</sup> of electrons liberated at that peak by liquor oxidation on the inert metal surface. The failure of the rest potential of steel to continue to drift upward beyond the anodic peak suggests that the concentration of oxidizing species is insufficient to consume this large current of electrons. Indeed, an analysis of the cathodic polarization curves in Fig. 46 suggests that the diffusion-limited current density (*i<sub>L</sub>*) for the available cathodic reaction is only about 1 mA/cm<sup>2</sup>. Thus, because of the anodic peak at +200 mV/Ag/Ag<sub>2</sub>S and the dearth of oxidizing species in the

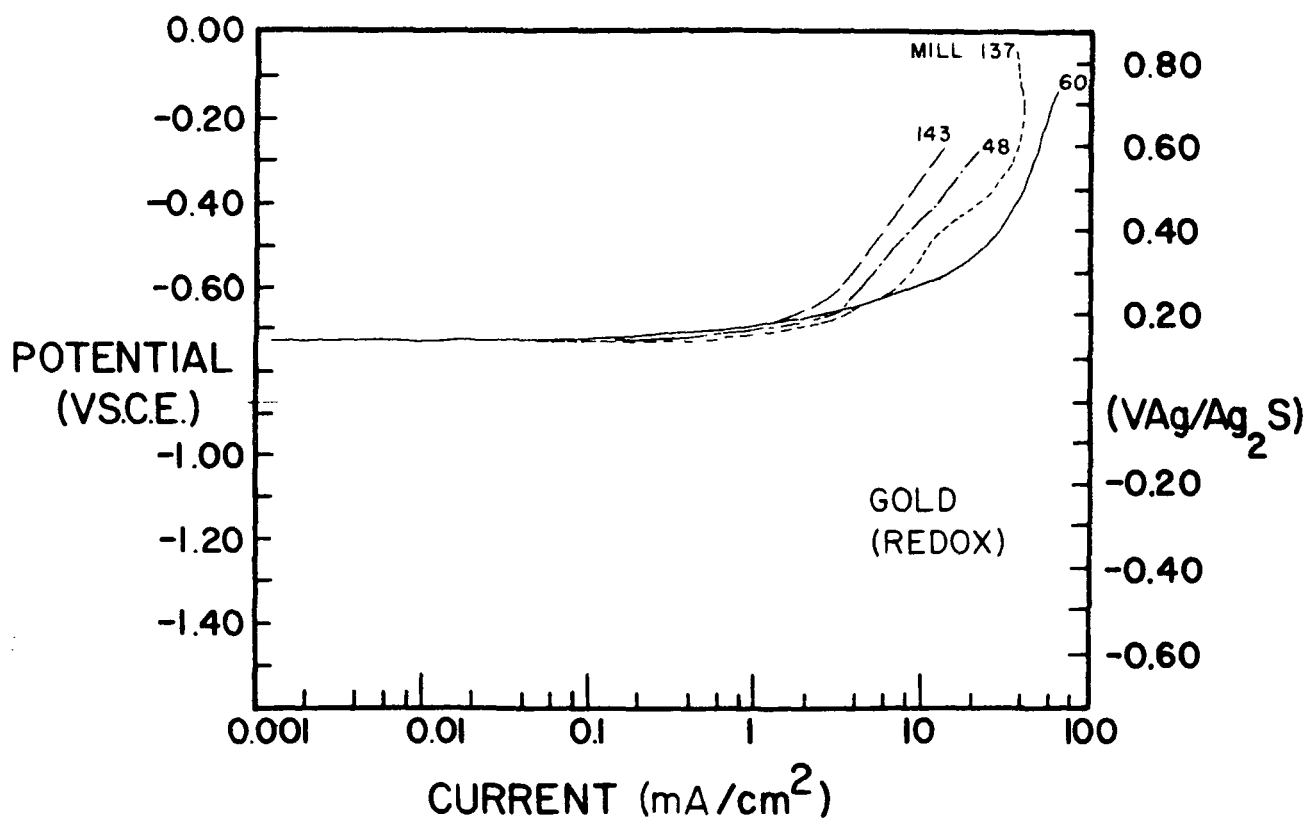


Figure 44. Anodic polarization curves on a gold electrode exposed to cooking liquors, showing a strong current above 200 mV Ag/Ag<sub>2</sub>S due to liquor oxidation.

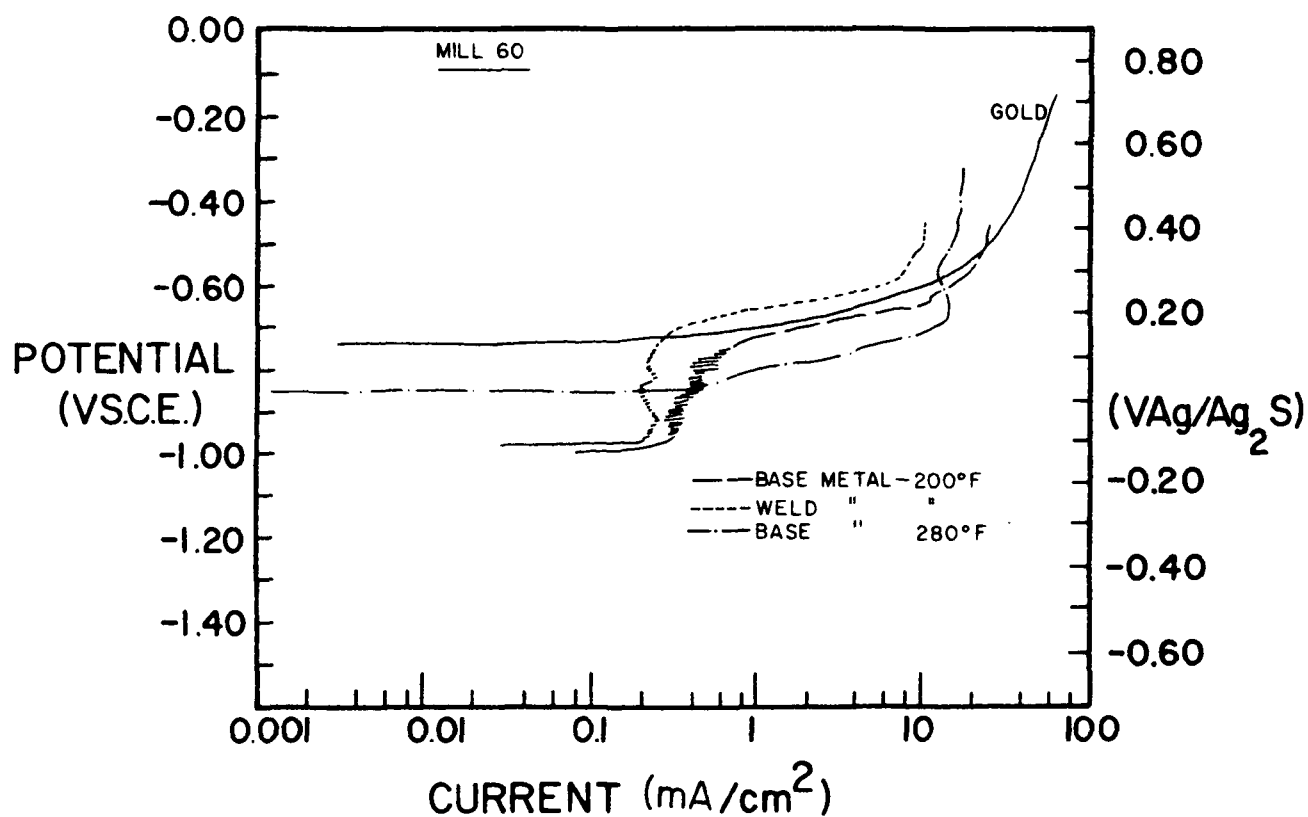


Figure 45. Anodic polarization curves for iron and gold electrodes showing a similar reaction above 200 mV Ag/Ag<sub>2</sub>S.

liquor, the potential of steel (and of gold) will be trapped below this anodic peak. That is, the rest potentials come to a stable position in the cracking range because the anodic reaction involving liquor oxidation acts as a ceiling for the upward drift of the rest potential.

The potential of the gold electrode is comfortably above the cracking range because it is a true redox electrode. The stable rest potential of the steel is somewhat lower because carbon steel has an additional anodic dissolution peak at  $\sim -30$  mV Ag/Ag<sub>2</sub>S. This peak is revealed when the steel surfaces are cleaned by hydrogen evolution for five minutes, followed by an anodic scan with the active steel surface. As shown in Fig. 47, a large anodic peak associated with the active-passive transition of iron occurs at  $-30$  mV Ag/Ag<sub>2</sub>S ( $-0.900$  VSCE), exactly as shown by Singbeil and Tromans (53-55). This anodic peak apparently contributes to the reactions that determine  $E_{\text{corr}}$  on a passive steel specimen, causing  $E_{\text{corr}}$  to fall in the cracking range, some 100 mV below the true redox potential.

Thus, it appears that the stable rest potential of steels exposed to cooking liquors will dwell in the cracking regime because cooking liquors, in contrast to pure caustic solutions, contain some chemical species that is electroactive in the range of normal potentials achieved by iron in caustic. Reactions involving this electroactive species place a ceiling on the upward drift of the rest potential of steel, causing the potential to reside in the danger zone for stress corrosion cracking. The stable rest potentials reside in the danger zone with liquors from both immune and susceptible mills, which dispels the notion the immune mills are immune because of their unique liquor chemistry.

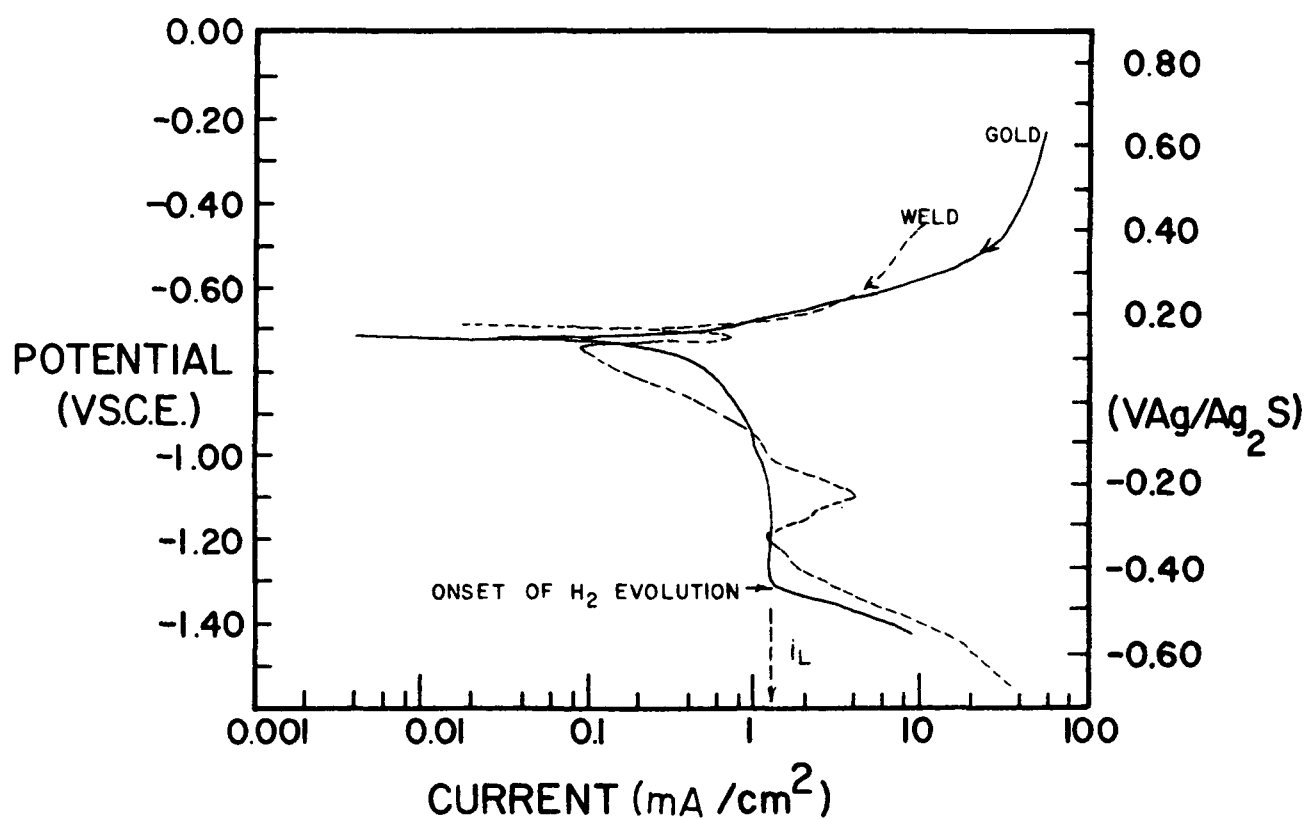


Figure 46. Analysis showing that the available cathodic current from liquor reduction is inadequate to allow an electrode to surmount the peak at 200 mV Ag/Ag<sub>2</sub>S.

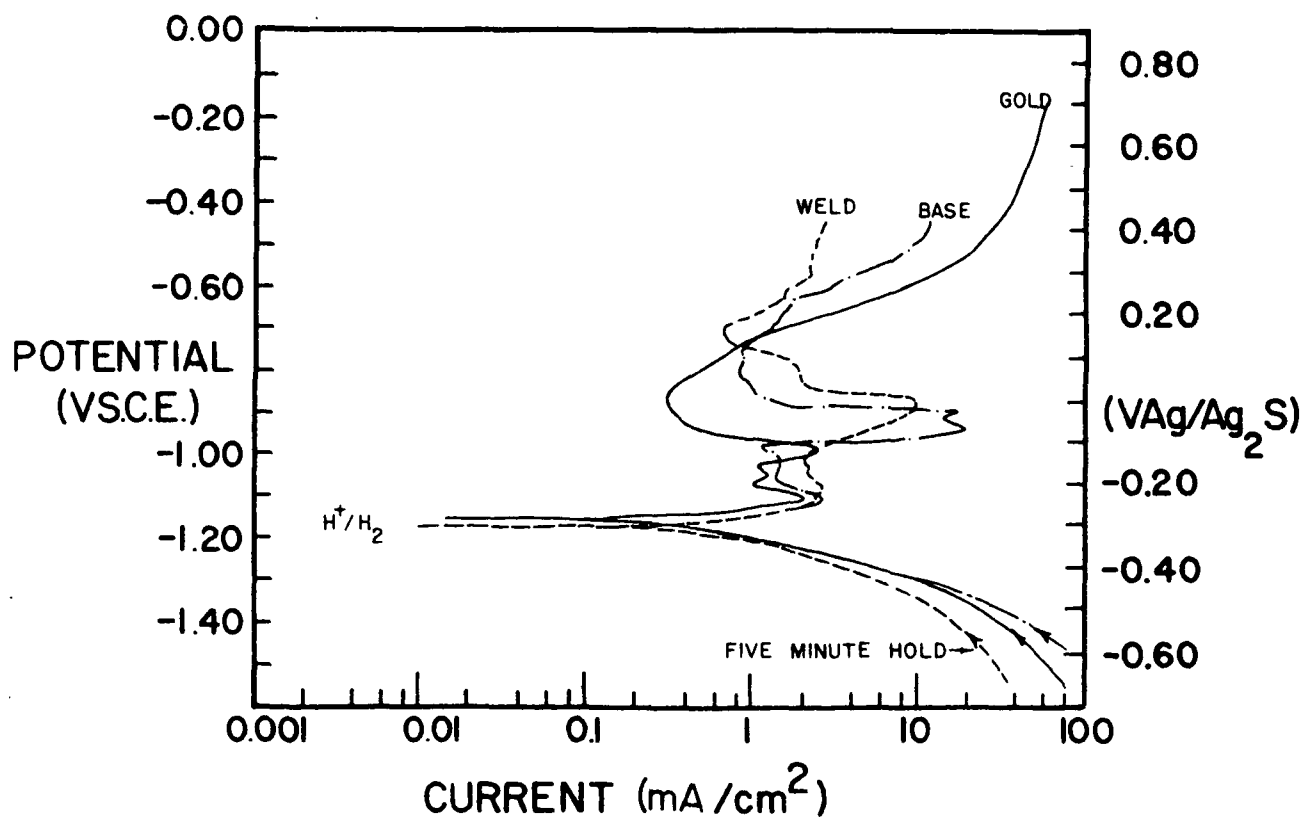


Figure 47. Anodic behavior of steel electrodes in makeup liquor following activation by hydrogen evolution at -600 mV  $\text{Ag}/\text{Ag}_2\text{S}$ .



### Corrosion Rates

The corrosion rates measured by the linear polarization method were initially quite high for the active steels, but soon fell to steady state values in the range 1-5 mils per year. The instantaneous corrosion rates were higher at higher temperatures, but fell to the steady state value more quickly than at the lower temperature, as would be expected from the passivation characteristics described above. There was no evidence of any significant differences in the corrosion rate of the base metals and weld metals studied.

### Ag/Ag<sub>2</sub>S Reference Electrode Calibration

As an aside, it is interesting to note that the transition from cathodic to anodic behavior (after a cleanup polarization of both steel and gold in the hydrogen evolution regime) occurs at the same potential, -300 mV Ag/Ag<sub>2</sub>S (-0.930 VSHE). This transition appears to be associated with the H<sub>2</sub>/H<sup>+</sup> reduction and oxidation half cell, whereby the hydrogen evolved on the electrode during cleanup is oxidized above E<sup>o</sup><sub>H<sup>+</sup>/H<sub>2</sub></sub>, regardless of the substrate material. Examples of the polarization curves corresponding to this reaction are shown in Fig. 47, when the present calibration of E<sub>Ag/Ag<sub>2</sub>S</sub> = -0.630 VSHE is used. This observation not only validates the use of a silver-silver sulfide reference electrode, but also indicates a procedure for obtaining a thermodynamically meaningful reference voltage for use as a benchmark in white liquor studies at elevated temperatures and pressures. This benchmark apparently can be obtained by electrolytically evolving hydrogen gas on the surface of an electrode and then executing a slow scan in the noble direction to determine the potential where the anodic oxidation of the gaseous hydrogen begins.

## Discussion

The chemical and electrochemical studies of cooking liquors have refined the understanding of the processes occurring during SCC of continuous digesters. For example, there do not appear to be any fundamental differences in the cooking liquor chemistries in the six immune and susceptible vessels. This result confirms the conclusions drawn from analysis of the statistics of liquor chemistries and cracking susceptibility. There also is no evidence for periodic swings through the potential range needed for cracking. Instead, the electrochemical studies show that the potentials drift to the danger zone and remain there, even in digester vessels without evidence of cracking. The characteristics of the cooking liquor are such that spontaneous departure from this potential regime where cracking can occur is unlikely.

Apparently, those mills that have avoided cracking in their digesters are fortunate to have either stresses below the threshold for cracking or a surface scale that restricts access of the electrolyte to the weldment surface. The exact reason for immunity of these vessels is not yet apparent.

With some added understanding of the electrochemistry of the SCC process, some alternative remedial measures might be considered that can force the rest potential from the regime where there is danger of caustic cracking. Certainly, anodic protection is a very attractive method for shifting the rest potential out of the danger zone, provided the durability of the system can be demonstrated. Perhaps, because the potential range where cracking is observed is apparently so narrow, slight cathodic polarization of the vessel might also be effective since large potential shifts will not be necessary. A penalty in higher corrosion rates would probably be paid with cathodic protection. It may

also be possible to force the rest potential out of the danger zone by the addition of more oxidizing species to the cooking liquor. If present in sufficient quantities, the ceiling at 200 mV Ag/Ag<sub>2</sub>S could be surpassed, and a spontaneous potential drift out of the danger zone might be possible. Polysulfide is an oxidizing species already present in liquors to some extent, and it is interesting to speculate on the possible advantages of increasing its concentration in cooking liquors as a means of avoiding continued caustic cracking.

A legitimate question yet to be addressed is the reason for the remarkable increase in digester cracking incidents if industry-wide changes in cooking liquor practices are not responsible. There may be several explanations for the apparent epidemic of digester cracking incidents. Perhaps the simplest explanation is that there were no incidents of cracking in the early years of Kamyr digester operation because few, if any, mills looked for cracking with the zeal shown in the post-Pine Hill era. Furthermore, there may be an unexplained incubation period for the onset of cracking that is now being completed for the numerous mills built in the mid-to-late 1960's. Even the most susceptible vessels apparently operated for more than ten years before cracking became evident, and for many vessels, that decade of incubation is drawing to an end. Moreover, the vintage digesters built in the late 1950's and early 1960's were nearly all stress relieved according to an early version of the ASME Code, and these vessels would be much more unlikely to crack during the early years of operation. Only now are we beginning to see the legacy of the change in the ASME Code.

Another interesting phenomenon related to the current cracking episodes is the possibility of nonpropagating cracks. To be sure, several vessels have

exhibited isolated deep cracks, but most of the cracking reported has been relatively shallow -- less than 1/4" deep in most cases, regardless of the length of exposure time. One wonders whether these cracks rapidly initiate and grow to a depth of about 1/4", followed by much slower growth or even cessation of growth. This would explain why a vessel inspected carefully after a decade of operation exhibits shallow cracks that reappear to the same depth after only one additional year. Perhaps rapid cracking is restricted to the last weld pass with much slower growth in the underlying passes that had been stress relieved by later passes. This may explain the apparent increase in cracking episodes in recently reinspected digesters.

## UNRESOLVED ISSUES

Inevitably, as a research program draws to an end, pivotal issues that cannot be addressed with time and funds available become more clearly defined. This certainly was the case for the present study, since the program was deliberately structured with a limited scope and short duration. While several questions have been resolved by this study, many unresolved questions remain to be addressed in subsequent studies. Some of these remaining issues are identified in this section.

Certainly, the central issue yet to be resolved is the reason for the different susceptibilities to cracking exhibited by different vessels. Based on current results, the susceptibility of a vessel to stress corrosion cracking is not simply related to some obvious detail of vessel fabrication or use, nor is susceptibility related to average white liquor compositions. The limited chemical analyses conducted during a few weeks of operation at a few mills in this study also failed to unearth a simple correlation between cracking susceptibility and liquor properties. The electrochemical studies conducted in this program may have changed the pivotal question from "Why do some vessels crack?" to "Why don't all vessels crack?", but the question remains unanswered.

In the absence of the simplest kind of correlations between cracking and digester characteristics, a more sophisticated approach to the issue would be required. Perhaps the link between cracking and digester operation is too subtle to be revealed unless multivariate analyses are performed which will show, for example, that only certain combinations of metallurgy, temperature, and liquor chemistry will cause cracking. On the other hand, cracking may be controlled by some quantity not considered in the present study -- for example,

the concentration of an organic compound derived from the low-temperature cooking process. Perhaps cracking occurs only intermittently during some upset condition or some nonroutine event in digester operation. At this stage, it is unclear whether any of these possibilities controls cracking susceptibility.

It is debatable whether the search for more subtle reasons for cracking susceptibility can be (or should be) pursued in view of diminishing returns. The data base regarding digester fabrication and routine operation is probably inadequate to support much more complexity in the search for links between susceptibility and routine operation. The situation is even worse for non-routine events such as liquor excursions, thermal shocks, etc. -- this data base is virtually nonexistent. If there is no simple cause and effect relationship for cracking in digesters -- as the current study suggests -- it is questionable whether further effort should be expended to examine cracking statistics in search of a more complicated relationship between cracking and digester use.

Another question raised by the current study is the relevance of the electrochemical studies to the electrochemical behavior of actual vessels. The conclusion of the electrochemical studies is that carbon steels exposed to cooking liquors spontaneously achieve potentials in the range necessary for cracking. However, the differences between the in situ electrochemical tests and the actual conditions at the vessel must be recognized. The test coupons were only exposed to liquors for a fraction of the time a vessel spends in contact with liquors, so the long term behavior of carbon steels was not examined. The cooking liquors at the impregnation zone will have somewhat lower caustic concentration and higher organic loads than the makeup liquors used for the electrochemical studies at the mill sites. The role of the surface film

normally found on the inside of digester vessels was not considered. The range of potentials where cracking susceptibility was expected was based on laboratory studies in simulated liquors, rather than SCC tests in actual liquors. While these differences between actual and simulated conditions are thought to be of secondary importance, it is possible that the simulation of impregnation zone conditions may not be representative of actual conditions, and vessel walls might not respond as test coupons have responded.

The preponderance of shallow cracks in most vessels raises another intriguing question about the propagation of cracks. With notable exceptions, most of the cracking observed in vessels is less than 1/4 inch deep, regardless of exposure time. Even for vessels with a few deeper cracks of grade A severity, most of the cracks are less than 1/4 inch deep. In many cases, shallow cracks were found in vessels inspected carefully for the first time after many years of service, yet the same pattern of shallow cracking was found after only six months of additional exposure. This observation may be an indication of rapid initiation and early growth of a crack, followed by much slower average propagation of cracks deeper than 1/8 inch. Deeper cracks may be encountering a weld structure that is more resistant to crack growth due to the tempering effects of the subsequent passes. Alternatively, the residual stresses driving crack growth may be restricted to the surfaces of vessels, so that deep cracks propagate into areas where the driving force for continued growth is reduced.

Many other questions relevant to digester cracking remain unresolved. Some of these questions are listed below.

- (i) What are the magnitude and distribution of residual stresses in weldments, and what is their role in digester cracking?

- (ii) Do fatigue loads contribute to the growth of cracks at nozzles, downcomer supports, or girth and vertical welds?
- (iii) What is the role of organic species on cracking in kraft cooking liquors?
- (iv) Why do vessel size and throughput apparently affect cracking susceptibility?
- (v) What is the species involved in the redox reaction that restricts the upward drift of rest potentials of carbon steel, causing the potential to reside in the cracking regime?
- (vi) How do liquors entering the vessel differ from makeup liquors as a consequence of the brief, low-temperature cooking occurring in the top recirculation line?
- (vii) What is the long-term durability of various repair measures used to remedy vessel cracking?



## REFERENCES

1. S. Hudak and A. Saxena. Int. J. of Fracture. 14:453(1978).
2. R. N. Parkins. Fundamental Aspects of Stress Corrosion Cracking. NACE, Houston, 1969. p. 601.
3. C. S. Carter and M. V. Hyatt. Stress Corrosion Cracking and Hydrogen Embrittlement of Iron Base Alloys. NACE, Houston, 1977. p. 524
4. K. Bohnenkamp. Fundamental Aspects of Stress Corrosion Cracking. NACE, Houston, 1969. p. 374.
5. C. M. Hudgins, R. L. McGlasson, P. Mehdizadeh, and W. M. Rosborough. Corrosion. 22:238(1966).
6. L. M. Dvoracak. Corrosion. 26:177(1970).
7. G. B. Kahout and W. J. McGuire. Materials Protection. 7:17(1968).
8. M. Pourbaix. Lectures on Electrochemical Corrosion. Plenum Press, 1973. p. 44.
9. E. Snape. Corrosion. 23:154(1967).
10. R. S. Treseder and T. M. Swanson. Corrosion. 24:31(1968).
11. H. Ishizuka and K. Onishi. Japan Chem. Quart., 3, 2:30(1967).
12. J. F. Bates. Corrosion. 24:32(1968).
13. H. L. Logan and H. T. Yoken. Proc. 2nd Int. Conf. on Metallic Corrosion, NACE, 1963. p. 109.
14. M. F. Baldy. Corrosion. 13:263(1957).
15. J. M. Sutcliffe, R. R. Fessler, W. K. Boyd and R. N. Parkins. Corrosion. 28:313(1972).
16. R. N. Parkins. Corrosion Science. 20:147(1980).
17. R. N. Parkins, P. W. Slattery, and B. S. Poulson. Corrosion/81, Toronto. NACE. Paper No. 96, 1981.
18. T. Zakrocynski and R. N. Parkins. Corrosion Science. 20:723(1980).
19. G. Herbsleb, B. Pfeiffer, R. Popperling and W. Schwenk. Z. Werkstofftechnik. 9:1(1978).
20. K. J. Kessler and E. Wender-Kalsch. Werkstoffe und Korrosion. 28:78(1977).

21. E. Wender-Kalsch. Werkstoffe und Korrosion. 31:534(1980).
22. S. W. Parr. Bulletin #94 of the Engineering Experiment Station. University of Illinois, Urbana. Jan. 1, 1917.
23. S. W. Parr and F. Straub. Bulletin #177 of the Engineering Experiment Station. University of Illinois, Urbana. June 5, 1928.
24. H. W. Schmidt, P. J. Gegner, G. Heinemann, C. F. Pogacar and E. H. Wyche, Corrosion. 7:295(1951).
25. W. G. Ashbaugh. Chemical Engineering Progress. 66, 10:44(1970).
26. F. V. Lyle, A. J. Bursle, H. C. Burghard, Jr. and G. R. Leverant. Corrosion/80, Chicago. NACE. Paper No. 233: 1980.
27. T. G. McCord, B. W. Bussert, R. M. Curran and G. C. Gould. Materials performance. 15, 2:25(1976).
28. F. K. Naumann and F. Spies. Praktische Metallographie. 7:637(1970).
29. V. I. Artem'ev, et al. Protection of Metals. 15, 1:45-8(1979).
30. F. A. Champion. Chem. Ind. 13:967(1957).
31. Corrosion Data Survey. NACE, Houston, TX. 1967.
32. J. E. Reinoehl and W. E. Berry. Corrosion. 28, 4:151(1972).
33. H. Graefen. Werkstoffe und Korrosion. 20:305(1969).
34. C. D. Weir. Proc. Inst. Mechanical Engineers (London). 163:18(1950).
35. F. P. A. Robinson and L. G. Nel. Proc. 2nd Int. Conf. on Metallic Corrosion. New York, NACE. 1963. 172 p.
36. A. A. Berk and W. F. Waldeck. Chemical Engineering. June, 1950. 235 p.
37. H. Mazille and H. H. Uhlig. Corrosion. 28:428(1972).
38. F. P. A. Robinson and L. G. Nel. Proc. 2nd Int. Conf. on Metallic Corrosion. New York, NACE. 1963. 172 p.
39. D. Singbeil and D. Tromans. Metallurgical Transactions 13A:1091(1982).
40. W. E. Berry. 5th Symposium on Line Pipe research. American Gas Association. 1974.
41. R. P. Harrison, D. DeG. Jones and J. F. Newman. Stress Corrosion Cracking and Hydrogen Embrittlement of Iron Base Alloys. NACE, Houston. 1969. 659 p.

42. M. J. Humphries and R. N. Parkins. Corrosion Science. 7:747(1967).
43. M. Pourbaix. Atlas of Electrochemical Equilibria in Aqueous Solutions. NACE, Houston. 1974.
44. R. B. Diegle and D. A. Vermilyea. J. E. Chem. Soc. 122:180(1975).
45. M. Hugo, J. Bellot, and E. Herzog. AGARD Conference Proceedings #98. Report AGARD-CP-98, NATO, 1972.
46. Z. N. Zhagalaya, I. I. Marchak, and R. K. Melekhov. Soviet Materials Science. 9, 3:342(1973).
47. R. B. Diegle and D. A. Vermilyea. Corrosion. 32:303(1976).
48. D. R. Johnston and T. G. McCord. Proc. 26th NACE Conf. NACE, Houston, TX. p. 227.
49. P. Hurst and H. C. Cowen. Nuclear Technology. 55:449(1981).
50. W. E. Schroeder, A. A. Berk and R. A. O'Brien. Met. and alloys. 8:320(1937).
51. R. Shalvoy, S. K. Duglin and R. J. Lindinger. Corrosion/81, Toronto. NACE 1981. Paper #9.
52. R. Parkins. Brit. Welding J. 1955. p. 495.
53. D. Singbeil and D. Tromans. J. E. Chem. Soc. 128:2065(1981).
54. D. Singbeil and D. Tromans. Pulp and paper industry corrosion problems, Vol. 3. NACE, Houston. 1982. p. 40.
55. D. Tromans. J. Electrochemical Society. 127:1253(1980).
56. D. Wensley and R. Charleton. Corrosion. 36:385(1980).
57. P. Doig and P. E. J. Flewitt. Metallurgical Transactions. 12A:923(1981).
58. Sven Rydholm. Pulping Processes. Interscience Publishers. New York.
59. Sven Rydholm. Continuous Pulping Processes. TAPPI Special Technical Publication No. 7, 1970.
60. H. MacLean and J. A. F. Gardner. Pulp and Paper Mag. Canada. 1953. p. 125.
61. J. W. Crellin. Proc. 68th Annual Meeting, CPPA. January 1982:A5.
62. B. Helberg. TAPPI 59, 5:52(1976).
63. Lockwood's Directory of the Paper and Allied Trades. Vance Publ. Co., New York, NY. 1982.

64. H. M. Cavanan and Z. S. Blanchard. TAPPI 52, 1:75(1959).
65. H. M. Cavanan and Z. S. Blanchard. TAPPI 57, 3:99(1974).
66. R. G. MacDonald and J. Franklin, eds. The Pulping of Wood. McGraw-Hill, New York, NY. 1969.
67. D. Wensley. Private communication.
68. R. J. Biernat and R. G. Robins. Electrochimica Acta. 17:1261(1972).
69. B. Haeglund and B. Roald. Norsk Skogindustri 351 (Oct. 1955).

#### ACKNOWLEDGMENTS

The assistance and cooperation of many individuals were instrumental in the successful completion of this program. Because of the severe time constraints, their efforts were frequently above and beyond the call of duty. Jim Tierney and Mike Heath conducted the bulk of the mill site experimental work. Bill Kreuger assisted in the design and construction of the apparatus. Mike Heath, Marcia Borchardt, LeRoy Borchardt, Sue Pociask, and Mary Block were involved in chemical analytical work.

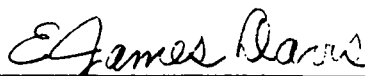
The cooperation of consultants, inspectors, insurers, and the personnel at the mill sites is also appreciated. Although they must remain anonymous, their help was absolutely vital in those areas of mill experimentation and questionnaire completion. Finally, the constructive comments of the DCRC Steering Committee Members were helpful and are much appreciated.

THE INSTITUTE OF PAPER CHEMISTRY



Ronald A. Yeske  
Senior Research Associate  
Engineering Division

Approved by:



E. James Davis  
Director  
Engineering Division

## APPENDIX

### ROUTINE DIGESTER OPERATION

Mill Site \_\_\_\_\_

#### 1. Overall Operation

- A. Rated Capacity \_\_\_\_\_ ADT/day      Average yield \_\_\_\_\_ %
- B. Average Production \_\_\_\_\_ ADT/day
- C. Changes in Avg. Daily Production \_\_\_\_\_  
\_\_\_\_\_
- D. Wood Species Pulped \_\_\_\_\_  
\_\_\_\_\_
- E. Major Changes in Wood Species Pulped? \_\_\_\_\_  
\_\_\_\_\_
- F. Kappa No. of Finished Pulp \_\_\_\_\_
- G. Other routine tests of pulp quality \_\_\_\_\_  
\_\_\_\_\_  
\_\_\_\_\_
- H. Recollection of unusual incidents in digester operation (e.g., serious overpressurization, high temperature excursions, etc.). Describe on back of page.
- I. Additions to digester other than chips, liquor. \_\_\_\_\_  
\_\_\_\_\_

#### 2. Pre-steaming

- A. Atmospheric pressure pre-steaming practiced \_\_\_\_ Y \_\_\_\_ N.
- B. Average residence time in steaming vessel \_\_\_\_\_ min.
- C. Steaming vessel inlet steam temperature \_\_\_\_\_ °F
- D. Steaming vessel Pressure \_\_\_\_\_ psi
- E. Average steam flow from flash tank to steaming vessel \_\_\_\_\_ lb/hr.
- F. Total steam flow to steaming vessel \_\_\_\_\_ lb/hr.
- G. Source of Steam to steaming vessel (other than the flash tank) \_\_\_\_\_  
\_\_\_\_\_

H. Venting practice to reduce non-condensibles in steaming vessel. \_\_\_\_\_

I. Average turpentine recovery \_\_\_\_\_ gal./day

J. Changes in pre-steaming operation \_\_\_\_\_

3. Chip Feed/Impregnation

A. What steps are taken to control chip level in the vessel \_\_\_\_\_

B. How is the chip level known? \_\_\_\_\_ Strain gage level sensors \_\_\_\_\_

Top separator screw torque \_\_\_\_\_ Other? \_\_\_\_\_

C. Estimate the distance from the bottom of the top separator to the top of the chips in normal operation \_\_\_\_\_ ft.

D. Normal top recirculation line temperature \_\_\_\_\_ °F

E. Normal make-up liquor temperature \_\_\_\_\_ °F

F. Causes and extent of temperature excursions in the vicinity of the top of the digester. \_\_\_\_\_

G. Top circulation flow rate Avg. \_\_\_\_\_ gpm

Max. \_\_\_\_\_ gpm

H. Average chip retention time in the impregnation zone (before cooking) \_\_\_\_\_ min.

I. Avg. white liquor flow rate from WL storage

\_\_\_\_\_ gal/min. Max. \_\_\_\_\_ gpm.

J. Average flow rate to chip chute from chip chute recirculation pump \_\_\_\_\_ gpm.

K. Use of any black liquor feed to cooking liquor? \_\_\_\_\_ Yes \_\_\_\_\_ No. Where added \_\_\_\_\_. Average flow rate \_\_\_\_\_ gpm.

- . Average temperature of make-up liquor \_\_\_\_\_ °F. Max. \_\_\_\_\_ °F.
- . Average temperature of white liquor from storage \_\_\_\_\_ °F Max. \_\_\_\_\_ °F
- . Impregnation zone temperature Avg. \_\_\_\_\_ °F Max. \_\_\_\_\_ °F
- . If analyses of make-up liquor, chip chute recirculation liquor, top recirculation liquor are available, please provide.

### Cooking

- . Temperature of upper circulation line (from vessel) Avg. \_\_\_\_\_ °F  
Max. \_\_\_\_\_ °F (to vessel) Avg. \_\_\_\_\_ °F Max. \_\_\_\_\_ °F
- . Temperature of lower circulation line. Avg. \_\_\_\_\_ °F  
Max. \_\_\_\_\_ °F (to vessel) Avg. \_\_\_\_\_ °F Max. \_\_\_\_\_ °F.
- . Flow rate in upper circulation line Avg. \_\_\_\_\_ gpm Max. \_\_\_\_\_ gpm.
- . Flow rate in lower circulation line avg. \_\_\_\_\_ gpm Max. \_\_\_\_\_ gpm.
- . Average residence time from upper cooking screen to lower extraction screen \_\_\_\_\_ hrs.
- . Average flow rate to flash tank #1 \_\_\_\_\_ gpm.
- . Average temperature weak black liquor to flush tank #1 \_\_\_\_\_ gpm.
- . Temperature in quench circulation line (from vessel) Avg. \_\_\_\_\_ °F  
Max. \_\_\_\_\_ °F (to vessel) Avg. \_\_\_\_\_ °F Max. \_\_\_\_\_ °F
- . Average flow rate in quench recirculation line \_\_\_\_\_ gpm.
- . Average (or target) active alkali in weak black liquor from flush tank 2 \_\_\_\_\_ g/l as chem/ $\text{Na}_2\text{O}$
- . Average (or target) sulfidity (AA basis) in weak black liquor from flash tank 2 \_\_\_\_\_ % on chem/ $\text{Na}_2\text{O}$  basis.
- . If analyses are available on black liquor from flash tank 2, please provide details.



5. Washing/Blowing

- A. Type of wash. \_\_\_\_\_ Countercurrent \_\_\_\_\_ Other \_\_\_\_\_
- B. Wash circulation pump flow rate \_\_\_\_\_ gpm
- C. Wash circulation temperature from vessel \_\_\_\_\_ °F. to vessel \_\_\_\_\_ °F.
- D. Source of wash water to cold blow pump \_\_\_\_\_ First stage wash filtrate  
 \_\_\_\_\_ Weak black liquor storage \_\_\_\_\_ other (describe) \_\_\_\_\_)
- E. Cold blow pump flow rate (average) \_\_\_\_\_ gpm.
- F. Cold blow inlet temperature \_\_\_\_\_ °F average.
- G. Pulp blow temperature \_\_\_\_\_ °F

6. Maintenance

- A. List items needing repeated replacement or repair and describe damage
- \_\_\_\_\_
- \_\_\_\_\_

- B. Acid cleaning of extraction screens.

- i) Frequency \_\_\_\_\_ times<sup>1</sup> per year
- ii) Acid used \_\_\_\_\_ Hydrochloric \_\_\_\_\_ Nitric \_\_\_\_\_  
 Sulfamic \_\_\_\_\_ Other ( )
- iii) Inhibitor used? Yes \_\_\_\_\_ No \_\_\_\_\_ Type \_\_\_\_\_  
 \_\_\_\_\_
- iv) Describe level of liquor in the digester during  
 acid cleaning. \_\_\_\_\_  
 \_\_\_\_\_
- v) Acid concentration \_\_\_\_\_% Inhibitor  
 concentration \_\_\_\_\_% pH \_\_\_\_\_
- vi) Average temperature of acid during cleaning  
 \_\_\_\_\_ °F
- vii) Are chips removed during cleaning? \_\_\_\_\_ Yes \_\_\_\_\_ No.
- viii) How are gases vented? \_\_\_\_\_  
 \_\_\_\_\_

ix) Are heater tubes bypassed during screens cleaning

Yes \_\_\_\_\_ No \_\_\_\_\_

x) Who does cleaning \_\_\_\_\_ Maintenance \_\_\_\_\_

Outside vender - Name \_\_\_\_\_

xi) Average acid consumption \_\_\_\_\_ gal.

xii) Pounds of metal removed \_\_\_\_\_

#### C. Heater Tube Cleaning/Descaling

i) Frequency \_\_\_\_\_ per year

ii) Type \_\_\_\_\_ Hydroblast \_\_\_\_\_ Acid Cook \_\_\_\_\_

other - \_\_\_\_\_

iii) Done by \_\_\_\_\_ Mill Maintenance \_\_\_\_\_ other

Company name \_\_\_\_\_

iv) Acid used, if any \_\_\_\_\_

v) Concentration \_\_\_\_\_ %

vi) Inhibitor \_\_\_\_\_ Name \_\_\_\_\_ Conc.

vii) Max. Temperature \_\_\_\_\_ °F

viii) Describe venting of gases produced \_\_\_\_\_

\_\_\_\_\_

#### D. Vessel Cleaning

i) Frequency

ii) Type \_\_\_\_\_ Acid Wash \_\_\_\_\_ Other \_\_\_\_\_

iii) Acid used: \_\_\_\_\_ Hydrochloric \_\_\_\_\_ Muriatic \_\_\_\_\_

Nitric \_\_\_\_\_ Sulfamic \_\_\_\_\_ Other \_\_\_\_\_

iv) Inhibitor used? Yes \_\_\_\_\_ No \_\_\_\_\_ Type \_\_\_\_\_

Conc. \_\_\_\_\_

v) Acid concentration \_\_\_\_\_ % pH \_\_\_\_\_

vi) Describe venting of vapors \_\_\_\_\_

\_\_\_\_\_

vii) Who does cleaning? \_\_\_\_\_

viii) Temperature of cleaning acid \_\_\_\_\_ °F

ix) Acid consumed \_\_\_\_\_ gal.

x) Metal loss \_\_\_\_\_ pounds

#### 7. Digester Start-up - Cold Start

A. Batch Cook Conditions \_\_\_\_\_ hrs. \_\_\_\_\_ °F

B. Cooking liquor used in batch \_\_\_\_\_ white liquor from storage, \_\_\_\_\_  
White/Black mixture \_\_\_\_\_ Other \_\_\_\_\_

C. Chip level during batch cook \_\_\_\_\_  
\_\_\_\_\_

D. Describe cooking liquor circulation during batch cook \_\_\_\_\_  
\_\_\_\_\_

E. Are chips steamed before batch cook \_\_\_\_\_ Y \_\_\_\_\_ N

F. How is liquor expansion accommodated during a batch cook? \_\_\_\_\_  
\_\_\_\_\_

G. Are non-condensable gases vented during batch cook? Yes \_\_\_\_\_ No \_\_\_\_\_

H. Is the vessel completely filled with liquid during batch cook?

Yes \_\_\_\_\_ No \_\_\_\_\_

I. How many cold starts are made in an average year? \_\_\_\_\_

How many in life of vessel? \_\_\_\_\_

J. What precautions, if any, are taken to limit the rate of temperature change  
of the vessel wall in the vicinity of the liquor inlets? \_\_\_\_\_  
\_\_\_\_\_

#### 8. Digester Shut-down

A. When shut-down, what is practice for the vessel lay-up?

\_\_\_\_\_ Fill with cold white liquor

\_\_\_\_\_ Fill with water (source \_\_\_\_\_)

\_\_\_\_\_ Acid clean and air dry

- \_\_\_\_\_ Air dry
- \_\_\_\_\_ Drain and close-surface moist
- \_\_\_\_\_ Fill with \_\_\_\_\_
- \_\_\_\_\_ Partially fill with \_\_\_\_\_
- \_\_\_\_\_ to level of \_\_\_\_\_

B. Approximately how many days has the vessel been shut-down since initial operation? \_\_\_\_\_

9. Miscellaneous

A. Describe any practices at this mill site which are unusual or different from those practiced at similar mills \_\_\_\_\_

\_\_\_\_\_

\_\_\_\_\_

B. Describe any extraordinary events in the operation of the digester system

\_\_\_\_\_

\_\_\_\_\_

\_\_\_\_\_

C. Describe any "hunches" why the vessel at this mill would be more or less susceptible to stress corrosion cracking of weldments \_\_\_\_\_

\_\_\_\_\_

\_\_\_\_\_

\_\_\_\_\_

D. Describe any significant changes in pulping operations at this mill site.

\_\_\_\_\_

\_\_\_\_\_

\_\_\_\_\_

## RECOVERY

### 1. Brown Stock Washing

A. Type Multistage Drum \_\_\_\_\_ Diffusion \_\_\_\_\_

Other \_\_\_\_\_

B. Manufacturer \_\_\_\_\_ Age \_\_\_\_\_

C. Wash Water Source \_\_\_\_\_  
\_\_\_\_\_

D. Wash Water Characteristics

	<u>inlet</u>		<u>outlet</u>
Avg. pH			
Max./Min. pH	/		/
Max./Min. Cl <sup>-</sup>	/	g/l	/ g/l
Avg. Cl <sup>-</sup>	/	g/l	g/l
Temp. Max./Avg./Min.	/ /		

E. Dilution factor (lb. H<sub>2</sub>O/lb AD stock) \_\_\_\_\_

F. Saltcake loss (lb. Na<sub>2</sub>SO<sub>4</sub>/ADT stock) \_\_\_\_\_

G. Additives used, function, product name \_\_\_\_\_  
\_\_\_\_\_

H. Changes in washing practice \_\_\_\_\_  
\_\_\_\_\_

I. Avg. residence time \_\_\_\_\_ Stage 1 \_\_\_\_\_ min.

Stage 2 \_\_\_\_\_ min.

Stage 3 \_\_\_\_\_ min.

### 2. Black Liquor Oxidation

A. Type: Strong \_\_\_\_\_ Weak \_\_\_\_\_ None \_\_\_\_\_

B. % Solids in liquor at oxidation \_\_\_\_\_ %

C. Oxidation Temperature \_\_\_\_\_ °F

D. Gas \_\_\_\_\_ O<sub>2</sub> \_\_\_\_\_ air

E. Oxygen/air consumption (lb/gal.) \_\_\_\_\_

F. Average retention time  $\frac{\text{vol.}}{\text{flow rate}} =$  \_\_\_\_\_

G. Residual sulfide \_\_\_\_\_ g/l as Na<sub>2</sub>O/chemical

H. Additives \_\_\_\_\_ Type, concentration, brand name \_\_\_\_\_

I. If available, describe composition of liquor before and after oxidation

J. Describe changes in BLOX \_\_\_\_\_

### 3. Evaporation

A. Number of effects \_\_\_\_\_ Age \_\_\_\_\_

B. Mfr. \_\_\_\_\_ Type: Long tube vertical \_\_\_\_\_

Horizontal Spray Film \_\_\_\_\_

Vertical Plate \_\_\_\_\_

C. Flow rate \_\_\_\_\_ gpm. in \_\_\_\_\_ gpm out

D. Max. steam inlet temp. \_\_\_\_\_ °F

E. Describe function, concentration, product name of additives used in evaporation \_\_\_\_\_

## F. Characteristics

<u>Effect</u>	<u>Inlet Solids (%)</u>	<u>Steam Inlet Temp. (°F)</u>
1A		
1B		
2		
3		
4		
5		
6		
7		

## G. Is a vapor recompression evaporator in use?

Yes \_\_\_\_\_ No \_\_\_\_\_ If yes, Mfr. \_\_\_\_\_

Age \_\_\_\_\_ Location \_\_\_\_\_

## H. Describe experience with evaporator tube scaling

<u>Effect</u>	<u>Scaling</u>	<u>Cleaning Frequency</u>	<u>Cleaning Method*</u>	<u>Type of Scale **</u>
1A				
1B				
2				
3				
4				
5				
6				
7				

\* H = hydroblast, A = Acid Boilout O = other (describe)

\*\* S = Sodium Sulfate, C = Calcium Carbonate, Si = Silicate, M = Mixed

## I. Composition of scale, if known. \_\_\_\_\_

\_\_\_\_\_

## J. Find concentration stage

If direct, \_\_\_\_\_ cascade \_\_\_\_\_ cyclone

If indirect \_\_\_\_\_ forced circulation, Rising film

\_\_\_\_\_ forced circulation, Flash

\_\_\_\_\_ Rising film

\_\_\_\_\_ Pre-heat, rising-falling film

\_\_\_\_\_ Rosenblad free flow

Mfr. \_\_\_\_\_

K. % solids into concentrator \_\_\_\_\_ %

L. % Solids out of concentrator \_\_\_\_\_ %

4. Tall Oil Recovery

	<u>Hardwood</u>	<u>Softwood</u>
A. Tall oil production (lb/day)	_____	_____
B. Avg. retention time in skim tank $\frac{\text{vol.}}{\text{flow rate}}$ min.	_____	_____
C. % solids at tall oil recovery	_____ %	_____ %
D. Temperature in skim tank	_____ °F	_____ °F
E. Acidulation of tall oil _____ Batch _____ Continuous		
i) pH during cook _____		
ii) temperature during cook _____		
iii) cooking time _____ hr.		
iv) acid used _____ $\text{H}_2\text{SO}_4$ _____ other		
v) acid source _____ $\text{ClO}_2$ generator _____ purchased		
vi) If purchased, name of supplier _____		
vii) Disposition of spent acid (brine) _____		
_____		
viii) Is NaOH purification practiced? Y _____ N _____		
ix) Is direct steam heating used _____ Y _____ N _____		
Source _____		



x) Source of acid dilution water in make-up tank

---

5. Recovery Boiler (one sheet for each boiler)

A. Number of recovery boilers \_\_\_\_\_ This is \_\_\_\_\_ of \_\_\_\_\_

B. Mfr. \_\_\_\_\_ B & W/CE \_\_\_\_\_ Other \_\_\_\_\_

C. Size \_\_\_\_\_ tons/day

D. Max. Steam temperature \_\_\_\_\_ °F Pressure \_\_\_\_\_ psi

E. Flue Gas temperature at Economizer \_\_\_\_\_ °F

F. Average O<sub>2</sub> in Flue Gas \_\_\_\_\_ %

G. Flue gas treatment

Precipitation: \_\_\_\_\_ Wet Bottom \_\_\_\_\_ Dry Bottom \_\_\_\_\_

Mfr. \_\_\_\_\_

Salt Production \_\_\_\_\_ ton/day

H. Liquor Feed:

i) From HBL storage \_\_\_\_\_ ton/day

ii) From saltcake make-up \_\_\_\_\_ ton/day

iii) % solids in HBL from storage \_\_\_\_\_ %

iv) % solids in HBL to boiler \_\_\_\_\_ %

v) Residual AA in HBL from storage \_\_\_\_\_ g/l  $\frac{\text{Na}_2\text{O}}{\text{Chem.}}$

vi) TTA in HBL \_\_\_\_\_ g/l as Na<sub>2</sub>O/Chemical

vii) Na conc. in HBL \_\_\_\_\_ g/l

viii) S in HBL \_\_\_\_\_ g/l

I. Is anything burned in the boiler besides kraft black liquor and start-up fuel? Describe \_\_\_\_\_

---

J. Salt cake make-up

From precipitator \_\_\_\_\_ lb./hr.

From ClO<sub>2</sub> process \_\_\_\_\_ lb./hr.

From tall oil recovery \_\_\_\_\_ lb./hr.

Purchased \_\_\_\_\_ lb./hr. Source \_\_\_\_\_

K. Other make-up chemicals \_\_\_\_\_

L. Average sodium recovery \_\_\_\_\_%

Average sulfur recovery \_\_\_\_\_%

M. Average % reduction  $\frac{\text{Na}_2 \text{ in smelt} \times 100}{(\text{Na}_2\text{S in Smelt}) + (\text{Na}_2\text{SO}_4 \text{ in smelt})}$  \_\_\_\_\_%

N. Min. % reduction \_\_\_\_\_%

Max. % reduction \_\_\_\_\_%

O. Black liquor Analysis (From Storage )/ (After saltcake)

i) $\text{Na}_2\text{CO}_3$	g/l or #ft. <sup>3</sup>	as $\text{Na}_2\text{O}$ /Chemical
ii) $\text{Na}_2\text{SO}_4$	g/l or #ft. <sup>3</sup>	$\text{Na}_2\text{O}$ /Chemical
iii) $\text{Na}_2\text{S}$	g/l or #ft. <sup>3</sup>	$\text{Na}_2\text{O}$ /Chemical
iv) $\text{Na}_2\text{S}_x$	g/l or #ft. <sup>3</sup>	$\text{Na}_2\text{O}$ /Chemical
v) $\text{Na}_2\text{S}_2\text{O}_3$	g/l or #ft. <sup>3</sup>	$\text{Na}_2\text{O}$ /Chemical
vi) $\text{Cl}^-$	g/l or #ft. <sup>3</sup>	$\text{Na}_2\text{O}$ /Chemical
vii) Calcium	g/l or #ft. <sup>3</sup>	$\text{Na}_2\text{O}$ /Chemical
viii) Magnesium	g/l or #ft. <sup>3</sup>	$\text{Na}_2\text{O}$ /Chemical
ix) Silica	g/l or #ft. <sup>3</sup>	$\text{Na}_2\text{O}$ /Chemical

P. Black Liquor Solids (To Furnace) (Before saltcake)

C \_\_\_\_\_%  $\text{H}_2$  \_\_\_\_\_% S \_\_\_\_\_%

$\text{O}_2 + \text{N}_2$  \_\_\_\_\_% Ash \_\_\_\_\_%

Q. Flue Gas analysis

$\text{O}_2$  \_\_\_\_\_%

$\text{CO}_2$  \_\_\_\_\_%

$\text{N}_2$  \_\_\_\_\_%

SO<sub>2</sub> \_\_\_\_\_%

R. Describe any changes in recovery practice \_\_\_\_\_

\_\_\_\_\_  
\_\_\_\_\_

6. Miscellaneous

A. Describe any additions to the recovery process not discussed above

(e.g., wash water steams, additives, etc. \_\_\_\_\_

\_\_\_\_\_  
\_\_\_\_\_

## RECAUSTICIZING

### 1. Dissolving Tank (use one form for each smelt tank if conditions differ at each)

A. Associated recovery boiler \_\_\_\_\_

B. Boiler type \_\_\_\_\_ B & W \_\_\_\_\_ CE \_\_\_\_\_ Other \_\_\_\_\_

C. Smelt throughput \_\_\_\_\_ tons smelt/day  
or \_\_\_\_\_ tons black liquor  
to boiler/day

D. Approximate tank size \_\_\_\_\_ Diam. x \_\_\_\_\_ high

E. Describe agitation system \_\_\_\_\_  
\_\_\_\_\_

F. Dissolving tank manufacturer/designer \_\_\_\_\_

G. Smelt stream breaker \_\_\_\_\_ steam from \_\_\_\_\_  
or \_\_\_\_\_ liquid from \_\_\_\_\_

H. Describe sites of possible air access to green liquor or smelt.

Inspection Port normally open? \_\_\_\_\_ Y \_\_\_\_\_ N

Air impingement from primary ports \_\_\_\_\_ Y \_\_\_\_\_ N

Vent stack damper/check valve \_\_\_\_\_ Y \_\_\_\_\_ N

Make-up liquid exposed to air \_\_\_\_\_ Y \_\_\_\_\_ N  
before arrival at

Air access to recirculating liquor \_\_\_\_\_ Y \_\_\_\_\_ N

I. Where does make-up liquid come from? \_\_\_\_\_  
\_\_\_\_\_

J. What is the composition of the make-up water? \_\_\_\_\_  
\_\_\_\_\_  
\_\_\_\_\_

K. What is flow rate from dissolving tank \_\_\_\_\_ gal/min.

L. What is recirculation flow rate? \_\_\_\_\_ gpm.

M. What additives are added to the dissolving tanks now or in the past. Please give specific product names \_\_\_\_\_

N. What is the green liquor composition?

	<u>Max.</u>	<u>Avg.</u>	<u>Min.</u>
$\text{Na}_2\text{S}$			as (g/l) (#ft. <sup>3</sup> ) and Chem./Na <sub>2</sub> O
NaOH			as (g/l) (#ft. <sup>3</sup> ) and Chem./Na <sub>2</sub> O
$\text{Na}_2\text{CO}_3$			as (g/l) (#ft. <sup>3</sup> ) and Chem./Na <sub>2</sub> O
$\text{Cl}^-$			as (g/l) (#ft. <sup>3</sup> ) and Chem./Na <sub>2</sub> O
$\text{Na}_2\text{S}_2\text{O}_3$			as (g/l) (#ft. <sup>3</sup> ) and Chem./Na <sub>2</sub> O
$\text{Na}_2\text{SO}_4$			as (g/l) (#ft. <sup>3</sup> ) and Chem./Na <sub>2</sub> O
$\text{Na}_2\text{S}_x$			as (g/l) (#ft. <sup>3</sup> ) and Chem./Na <sub>2</sub> O
$\text{Na}_2\text{SO}_3$			as (g/l) (#ft. <sup>3</sup> ) and Chem./Na <sub>2</sub> O
Total Titratable Alkalai			as (g/l) (#ft. <sup>3</sup> ) and Chem./Na <sub>2</sub> O
Active Alkalai			as (g/l) (#ft. <sup>3</sup> ) and Chem./Na <sub>2</sub> O
Sulfidity			% AA/TTA basis

O. What changes have been made in smelt dissolving practices \_\_\_\_\_

2. Green Liquor Clarifier (One form for each)

A. Number of clarifiers \_\_\_\_\_ Dregs \_\_\_\_\_ #/day

B. Size: \_\_\_\_\_ O.D. x \_\_\_\_\_ height. \_\_\_\_\_ vol.

C. Age. \_\_\_\_\_ Manufacturer \_\_\_\_\_

D. What dissolving tank feeds this clarifier? \_\_\_\_\_

E. Design: \_\_\_\_\_ Multiple trays \_\_\_\_\_ Single tray with storage \_\_\_\_\_

Other - \_\_\_\_\_

F. Number of trays \_\_\_\_\_

G. Is a supplementary filter used? \_\_\_\_\_ Y \_\_\_\_\_ N

Describe \_\_\_\_\_

- H. What is clarifier throughput \_\_\_\_\_ gpm.
- J. Is the liquid surface exposed to the air? \_\_\_\_\_ Y \_\_\_\_\_ N
- K. What is the temperature of the green liquor  
Avg. \_\_\_\_\_ °F Max. \_\_\_\_\_ °F Min. \_\_\_\_\_ °F
- L. Are dregs removed \_\_\_\_\_ continuously \_\_\_\_\_ intermittently
- M. Are additives used? (Defoamers, anti-scaling, etc.) Please describe by  
function and product name. \_\_\_\_\_  
\_\_\_\_\_
- N. What are current cleaning practices? \_\_\_\_\_  
\_\_\_\_\_
- O. Describe recent changes in design or operation of green liquor clarifiers  
\_\_\_\_\_  
\_\_\_\_\_

### 3. Slaker

- A. Age \_\_\_\_\_ Temperature \_\_\_\_\_ Avg. \_\_\_\_\_ Max. \_\_\_\_\_ Min. \_\_\_\_\_
- B. Manufacturer \_\_\_\_\_
- C. Number of slakers \_\_\_\_\_
- D. Describe any differences in operation of different slakers \_\_\_\_\_  
\_\_\_\_\_
- E. What is flow rate of green liquor into each slaker in gpm \_\_\_\_\_
- F. What is the total lime consumed per day \_\_\_\_\_
- G. Are additives used in the slaker? Please describe by function and product  
name \_\_\_\_\_  
\_\_\_\_\_
- H. What is total lime feed rate from kiln \_\_\_\_\_ tons/day.
- I. What is the rate of make-up lime \_\_\_\_\_ tons/day.
- J. Where does make-up lime come from? \_\_\_\_\_  
\_\_\_\_\_

- K. What is the average storage time for lime? \_\_\_\_\_ hrs.
- L. What is green liquor to lime ratio \_\_\_\_\_ gal. / \_\_\_\_\_ ton.
- M. What dregs production rate \_\_\_\_\_ #/day
- N. What changes have been made in slaking practice ? \_\_\_\_\_
- 

4. Causticizers

- A. Number in series \_\_\_\_\_
- B. Average residence time \_\_\_\_\_
- C. Total solids in outlet flow \_\_\_\_\_ g/l
- D. Describe function and product name of any additives used \_\_\_\_\_
- 
- E. Temperature at Inlet: Avg. \_\_\_\_\_ °F Max. \_\_\_\_\_ °F Min. \_\_\_\_\_ °F

5. White Liquor Clarifiers (one form for each)

- A. Number of clarifiers \_\_\_\_\_ This one is # \_\_\_\_\_ of \_\_\_\_\_
- B. Age \_\_\_\_\_ Manufacturer \_\_\_\_\_ Size \_\_\_\_\_ OD x \_\_\_\_\_ Ht.
- C. Design: \_\_\_\_\_ Single tray with storage  
\_\_\_\_\_ Multiple tray (#of trays \_\_\_\_\_)  
\_\_\_\_\_ Other \_\_\_\_\_
- D. Is a belt filter or other in-line filter used? No \_\_\_\_\_ Yes \_\_\_\_\_ Type \_\_\_\_\_
- E. Throughput \_\_\_\_\_ gpm
- F. Does liquor contact air in feedbox, outlet, tank top? Circle if "yes"
- G. Temperature: Avg. \_\_\_\_\_ °F Max. \_\_\_\_\_ °F Min. \_\_\_\_\_ °F
- H. Total solids in white liquor in \_\_\_\_\_ g/l
- I. Total solid in white liquor out \_\_\_\_\_ g/l

## J. White liquor composition out

	<u>Max.</u>	<u>Avg.</u>	<u>Min.</u>	
NaOH				in (g/l) (#ft. <sup>3</sup> ) as (Chem.) (Na <sub>2</sub> O)
Na <sub>2</sub> S				in (g/l) (#ft. <sup>3</sup> ) as (Chem.) (Na <sub>2</sub> O)
Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub>				in (g/l) (#ft. <sup>3</sup> ) as (Chem.) (Na <sub>2</sub> O)
Na <sub>2</sub> SO <sub>4</sub>				in (g/l) (#ft. <sup>3</sup> ) as (Chem.) (Na <sub>2</sub> O)
Na <sub>2</sub> SO <sub>3</sub>				in (g/l) (#ft. <sup>3</sup> ) as (Chem.) (Na <sub>2</sub> O)
Na <sub>2</sub> CO <sub>3</sub>				in (g/l) (#ft. <sup>3</sup> ) as (Chem.) (Na <sub>2</sub> O)
Na <sub>2</sub> S <sub>x</sub>				in (g/l) (#ft. <sup>3</sup> ) as (Chem.) (Na <sub>2</sub> O)
Cl <sup>-</sup>				in (g/l) (#ft. <sup>3</sup> ) as (Chem.) (Na <sub>2</sub> O)
Other?				in (g/l) (#ft. <sup>3</sup> ) as (Chem.) (Na <sub>2</sub> O)
TTA				in (g/l) (#ft. <sup>3</sup> ) as (Chem.) (Na <sub>2</sub> O)
AA				in (g/l) (#ft. <sup>3</sup> ) as (Chem.) (Na <sub>2</sub> O)
Sulfidity				% as Chem./Na <sub>2</sub> O AA/TTA basis

K. Causticizing efficiency  $\frac{(\text{NaOH as Na}_2\text{O})}{\text{NaOH as Na}_2\text{O} + (\text{Na}_2\text{CO}_3 \text{ as Na}_2\text{O})} \times 100$

Avg. \_\_\_\_\_% Max. \_\_\_\_\_% Min. \_\_\_\_\_%

L. Lime mud removal \_\_\_\_\_ Continuous \_\_\_\_\_ Intermittent

M. Please describe any additives used, by function, amount, and product name

\_\_\_\_\_

\_\_\_\_\_

N. Average residence time in clarifier  $\left( \frac{\text{vol.}}{\text{flow rate}} \right) = \text{_____ min.}$

O. Describe any corrosion-related problems with WL clarifiers \_\_\_\_\_

\_\_\_\_\_

P. Suspended solids in outlet white liquor \_\_\_\_\_ g/l

Q. Describe changes in W.L. processing \_\_\_\_\_

\_\_\_\_\_

\_\_\_\_\_

\_\_\_\_\_



6. White Liquor Storage (one form for each tank)

- A. No. of white liquor storage tanks \_\_\_\_\_
- B. This is for \_\_\_\_\_ of \_\_\_\_\_. Age \_\_\_\_\_
- C. Size \_\_\_\_\_ Diam. x \_\_\_\_\_ Mfr. \_\_\_\_\_
- D. Temperature? \_\_\_\_\_ °F Avg. \_\_\_\_\_ °F Max. \_\_\_\_\_ °F min.
- E. Average residence time  $\frac{\text{vol.}}{\text{flow rate}}$  = \_\_\_\_\_ min.

7. Lime Mud Washing

- A. Volume \_\_\_\_\_ tons/day
- B. % solids out of W.L. clarifier
- C. Washer water source and composition \_\_\_\_\_  
\_\_\_\_\_
- D. Lime mud washer: Type \_\_\_\_\_  
Mfr. \_\_\_\_\_ Age \_\_\_\_\_
- E. Lime mud filter: Type \_\_\_\_\_  
Mfr. \_\_\_\_\_ Age \_\_\_\_\_
- F. Describe additives used, function, concentration and brand name  
\_\_\_\_\_  
\_\_\_\_\_
- G. Lime mud composition \_\_\_\_\_  
\_\_\_\_\_
- H. Residual  $\text{Na}_2\text{O}$  \_\_\_\_\_ %
- I. Disposition of wash water \_\_\_\_\_
- J. Is a tray thickener used? Yes \_\_\_\_\_ No \_\_\_\_\_
- K. Describe changes in operation of lime mud washers \_\_\_\_\_  
\_\_\_\_\_

## 8. Lime Kiln

- A. Type: ☐ Rotary ☐ Fluidized Bed
- B. Manufacturer \_\_\_\_\_ Age. \_\_\_\_\_
- C. Capacity \_\_\_\_\_ tons/day
- D. Make-up: Limestone \_\_\_\_\_ ton/day  
Lime \_\_\_\_\_ ton/day
- E. Make-up source \_\_\_\_\_
- F. Fuel type \_\_\_\_\_ Consumption \_\_\_\_\_
- G. Exit gas temperature \_\_\_\_\_ °F
- H. Max. kiln temperature \_\_\_\_\_ °F
- I. Gas Scrubber, used? Wet ☐ Dry ☐ None ☐
- J. Retention time  $\left( \frac{11.2 \times \text{length (ft.)}}{\text{slope (deg)} \times \text{rpm} \times \text{I.D. (ft.)}} \right) =$  \_\_\_\_\_
- K. O<sub>2</sub> concentration in ex. + gas \_\_\_\_\_%
- L. Efficiency (Btu/ton of product) = \_\_\_\_\_

## 9. Miscellaneous

- A. List function, concentration, product name for any additives to recausticizing system not described above. For example, defoamers, sedimentation aids, polymers, corrosion inhibitors, scale inhibitors, etc. Also list those additives previously used, if known.

---

- B. List any additional source of water added to the recausticizing system not described above. \_\_\_\_\_
- C. What quality control checks are run on white liquor.

How often?